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ALLEN'S
COMMERCIAL ORGANIC ANALYSIS

FOURTH EDITION

In many respects this edition of Allen will be a new work. The field of Commercial Organic Analysis has been so enlarged and specialised during the last few years that it was found necessary to rewrite many parts and add much new matter. Obsolete methods are omitted; what little of the old text remains has been carefully revised and many new illustrations added.

To accomplish the object in view, namely, the furnishing of a modern work of the greatest practical value to the analyst, it was deemed advisable to secure the services of an English and an American editor and to organise a corps of writers particularly versed in the subjects discussed. Aside from those who have written for this volume, the following gentlemen have promised to write or revise articles for the forthcoming ones: J. A. Gardner, Chemical Department, St. George's Hospital, London; A. Marshall, Chief Inspector of Explosives, Indian Army; A. H. Gill, Massachusetts Institute of Technology, Boston; F. C. Garrett, Armstrong College, Newcastle-on-Tyne; Samuel S. Sadtler, Philadelphia; C. A. Mitchell, London; Leonard Archbutt, Derby; C. A. Klein, London; William Robertson, London; W. P. Dreaper, author of "The Chemistry and Physics of Dyeing"; Cecil Revis, London; Edward Horton, Chelsea; Dr. M. B. Blackler, Ilford; E. W. Lewis, Laughton; J. Merritt Matthews, formerly Professor of Chemistry and Dyeing, Philadelphia Textile School; Dr. T. M. Lowry, London; E. J. Parry, London; Charles H. LaWall, Assistant in Theory and Practice of Pharmacy, Philadelphia College of Pharmacy; J. T. Hewitt, Surbiton; W. M. Gardner, Technical College, Bradford; Percy H. Walker, Washington; A. F. Seeker, New York.

The general arrangement of the volumes remains as before, only such changes have been made as will bring the text into line with the latest scientific classification. Great care has been exercised by the editors and contributors in the choice of methods and only those of the highest degree of accuracy and rapidity selected. Effort has been made to secure uniformity in weights and measures, nomenclature and abbreviations. References are to original sources, not to translations or abstracts.

The work will be issued in eight volumes, numbered consecutively, and will be published as rapidly as possible. Volumes I and II are ready; Volumes III and IV will be published very shortly; the remainder will follow as quickly as is consistent with good work.

The Publishers.

See next page for detail announcement.

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ALLEN'S
COMMERCIAL ORGANIC ANALYSIS

VOLUME II

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ALLEN'S COMMERCIAL
ORGANIC ANALYSIS

A TREATISE ON

THE PROPERTIES, MODES OF ASSAYING, AND PROXIMATE
ANALYTICAL EXAMINATION OF THE VARIOUS
ORGANIC CHEMICALS AND PRODUCTS
EMPLOYED IN THE ARTS, MANUFACTURES, MEDICINE, Etc.

WITH CONCISE METHODS FOR

THE DETECTION AND ESTIMATION OF THEIR IMPURITIES,
ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION

VOLUME II

Fixed Oils, Fats and Waxes, Special Characters and Methods, Butter
Fat, Lard, Linseed Oil, Higher Fatty Acids, Soap, Glycerol,
Cholesterols, Wool-fat, Cloth Oils

BY THE EDITORS AND THE FOLLOWING CONTRIBUTORS

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FOURTH EDITION. ENTIRELY REWRITTEN

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PREFACE

In the preparation of the present volume, the same methods have been adopted as in the case of the first volume of this edition. The greater proportion of the subject matter was included in Vol. 2, part 1, of the third edition of "Commercial Organic Analysis," but the analytical chemistry of explosives, partly included in that volume and partly in Vol. 1 of the same edition, will appear in a later volume.

All parts of the book have been revised by those especially qualified for the work; the text has been completely rewritten, and a very large amount of new matter has been added.

The editors desire to thank the contributors for the care and attention given in the preparation of the articles.

As usual, unless otherwise noted, temperatures are centigrade.

March, 1910.

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FIXED OILS, FATS, AND WAXES.

By C. AINSWORTH MITCHELL, B. A. (Oxon.), F. I. C.

GENERAL PROPERTIES AND ANALYTICAL METHODS.

Under the names of fixed oils, fatty oils, fats, and waxes are classed many substances occurring in animal and vegetable structures.

The term fixed or fatty oil is generally used for such members of the group as remain liquid at ordinary temperatures. Those having this character contain a relatively large proportion of olein or other compounds of low m. p., but beyond this there is no absolute distinction between fixed oils and fats.

The waxes possess well-defined physical characters, and differ in chemical composition from the true fats. They are, however, in many respects closely related to them, and are conveniently described in the same division.

The following are the general properties characterising the true fats and fixed oils:

1. When pure, most of them are colourless or pale yellow. Impure and commercial oils vary in colour from light yellow to red, and even to brown and black. Many vegetable oils have a distinct shade of green from the presence of chlorophyll, and show absorption spectra, which is never the case with oils of animal origin.

2. Their smell and taste are often peculiar, and are characteristic of their origin. As these characters become less perceptible the more completely the oil is purified, they may be due to the presence of associated foreign matters not readily removed, rather than to the constituents of the oil.

3. If dropped in a liquid condition on paper they leave a permanent grease-spot, unless they are crystalline and hard enough to be rubbed off.

4. They are not fluorescent and, as a rule, have but little rotatory action on a ray of polarised light. Castor and croton oils, however, are dextrorotatory.

5. The sp. gr. is less than that of water, ranging between the limits of 0.875 and 0.970; but if certain anomalous oils from marine animals be excluded, the lowest density is about 0.912 at a temperature of 15° C. In the fluid state, at the temperature of boiling water, the sp. grs. range from 0.850 to about 0.910. The waxes and allied substances are still lighter in the melted condition their sp. gr. ranging from 0.808 to 0.845.

6. The fusing or melting points range within wide limits, and are liable to modification in an obscure manner by special treatment.

7. They are practically insoluble in water, but dissolve to some extent in absolute alcohol or strong spirit, especially when hot, and are readily soluble in ether, chloroform, carbon tetrachloride, carbon disulphide, benzene, petroleum spirit, turpentine, and other volatile solvents. They are readily miscible with one another.

8. The fixed oils and fats are composed of carbon, hydrogen, and oxygen, the nitrogen, sulphur, phosphorus, and iron present in many of them being due to foreign matters, which often cannot be completely removed.

9. They do not emit inflammable vapours at the ordinary temperature, but may be burnt by means of a wick. They are not capable of being distilled at the ordinary atmospheric pressure without decomposition. When heated alone they darken and evolve acrid offensive vapours; and when further heated to about 315° carbon dioxide is evolved, together with the peculiarly irritating vapours of acrolein, C_3H_4O, various volatile organic acids, and gaseous, liquid, and solid hydrocarbons. The temperature at which this decomposition occurs has been improperly called the "boiling point" of the oil, the phenomenon of apparent ebullition being really due to the escape of the gases formed by the decomposition.

10. On distillation with superheated steam, they undergo a simpler decomposition, with formation of glycerol and fatty acids. This change may also be effected by acting on them with sulphuric acid or a strong base. The action is known as "saponification," or hydrolysis and its analytical application is discussed in another section.

11. If air is excluded, the fixed oils may be preserved unchanged for a lengthened period, but, on exposure to air, many of them thicken owing to absorption of oxygen, and are ultimately converted (if exposed in sufficiently thin layers) into a yellowish transparent skin or

varnish.[1] Such oils (*e. g.*, linseed, walnut, hempseed, and poppy-seed oils) are called *drying oils*.

12. The *non-drying oils* behave in a different manner on exposure to air. They gradually become *rancid;* that is, lose their colour (and to a certain extent their fluidity), and acquire an acrid, disagreeable taste, and acid reaction to litmus-paper. This alteration is primarily an oxidation process brought about by the action of air and light, and is accompanied by the liberation of free fatty acids and other bodies. It may be accelerated by the presence of foreign matters, such as the cellular substance of the animal or plant from which the oil was extracted. These substances furnish nourishment for bacteria, which probably cause further changes when once the decomposition process has begun. By agitating such rancid oil with hot water, and subsequently treating it with a cold and dilute solution of sodium carbonate, the products of decomposition may often be removed and the fat restored to its original state.

EXTRACTION AND PURIFICATION OF FIXED OILS AND FATS.

The method of extraction and subsequent treatment have considerable influence upon the analytical characteristics of the product. For the *extraction* of oils and fats from animal tissues it is often sufficient to allow the material (*e. g.*, cod liver) to become somewhat putrid, when some of the oil drains from it, or may be obtained by slight pressure. A further quantity can be extracted by warming or boiling the tissue with water, as is done with blubber. In the case of lard and tallow, it is merely necessary to heat the substance alone, and strain the melted fat away from the membranous matter. From compact tissue, such as bone, the whole of the fat can be extracted by a solvent only.

The extraction of the fat or oil from vegetable tissue may be effected by boiling the crushed substance with water or by subjecting it to powerful pressure, either at the ordinary temperature or between plates heated to slightly above the m. p. of the fat. The product obtained in the last manner will usually contain more "stearin" or solid fat than the "cold-drawn" oil. In either case a certain quantity of the fat is mechanically retained by the tissues, and hence a larger yield can be obtained by the use of carbon disulphide or petroleum spirit, which, on being distilled off, leaves the fat behind.

---

[1] Under certain conditions, as when cotton-waste, shoddy, or hemp is moistened with oil and exposed to the air, the oxidation of the oil becomes so energetic as to lead to considerable elevation of temperature, and even actual inflammation (see p. 38).

The proportion of oil or fat yielded by any particular material depends on many conditions.

Tables of the yields usually obtained from different seeds, nuts, etc., are given in Schaedler's *Untersuchungen der Fette, Oele und Wachsarten*, 1892, p. 25, and in Wright and Mitchell's *Oils, Fats and Waxes*, 1903, 297.

Oils obtained by the use of solvents are more likely to contain impurities than those obtained by pressure.

Estimation of Oils and Fats.—In the laboratory, the estimation of the oil in solid animal and vegetable matters is effected by treating the finely divided and previously dried substance[1] with a suitable solvent under such conditions as to ensure complete extraction. Carbon disulphide or petroleum spirit may be employed for the purpose, but ether or carbon tetrachloride is, as a rule, preferable.

The *exhaustion* of seeds, bones, shoddy, oil-cakes, milk residues, etc., by simply digesting the substance with the solvent at the ordinary temperature, with frequent agitation, in a closed flask, is unsatisfactory, as it requires a considerable quantity of the solvent, of which a notable proportion is likely to be lost. The apparatus devised by Szombathy (see Vol. 1, p. 77) obviates these drawbacks. The substance to be exhausted of oil is enclosed in a plaited filter or cylinder of filter-paper; or if it be coarse, it is sufficient to place it loose in a large test-tube having an aperture at the bottom closed by a plug of glass-wool.

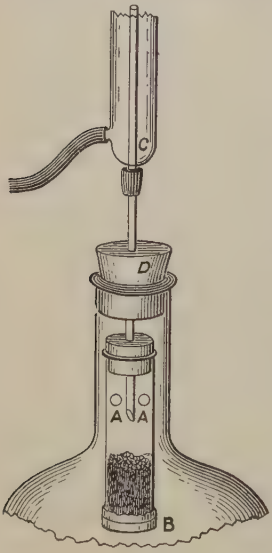

FIG. 1.

A very simple and convenient form of exhauster, adapted either for extraction or re-percolation, has been described by Dunstan and Short (*Pharm. J.*, [3], 1882, **13**, 664).

A form of exhauster (Fig. 1), suitable for the extraction of very small quantities of material, was devised by West-Knights (*Analyst*, 1883, **8,** 65). It has the advantage of being readily constructed in the laboratory. A percolator is made by cutting off the bottom from a test-tube of suitable size, and blowing a hole or two (A A) in the side of the tube about an inch from the top. A disc of filter-paper or fine cambric (B) is tied over the lower end of the tube. The substance to be extracted is placed in the tube, and kept in its place by some glass-wool or a perforated disc of metal, and the tube with its contents then fixed by a cork to the lower end of the tube of a vertical condenser (C). This is fitted by a larger cork (D) to the neck of an ordinary flask containing the volatile solvent. On heating the flask the vaporised solvent passes through the holes in the side of the test-tube up into the tube of the condenser, where it is liquefied. The condensed liquid drops back into the test-tube, percolates through the substance to be extracted, and falls to the bottom of the flask, to be again volatilised. As the percolator is inside the flask, its contents are kept constantly at the b. p. of the solvent, and, the action being continuous and automatic, very rapid exhaustion may be effected.

---

[1] In the case of linseed and other substances containing drying oils, the desiccation must either be omitted or conducted in an atmosphere of hydrogen or illuminating gas.

Other forms of exhauster have been contrived by Church, Drechsel, Angell, Thoms, Thresh (*Pharm. J.*, [3], 1884, **15,** 281); Frühling (*Zeit. angew. Chem.*, 1889, 242). (See also Vol. 1.)

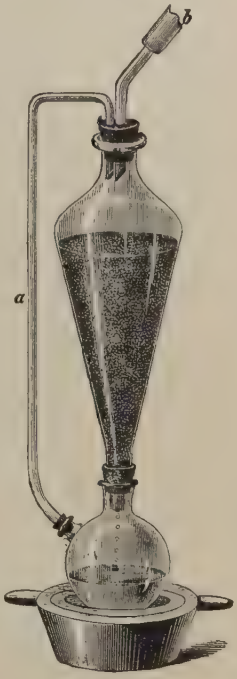

FIG. 2.

To *recover* the oil from its solution in the ether or other liquid employed, the solvent should be distilled off at a steam-heat, and the last traces of it removed by placing the flask on its side and heating it in the water-oven until constant in weight. In some cases the complete removal of the solvent is best effected by blowing a gentle stream of air, previously filtered through cotton-wool, through the flask while it is maintained at a temperature of 100°.

Large quantities of material may be readily extracted in the apparatus (Fig. 2), which is constructed on the principle of the Szombathy extractor.

In the case of *liquids* containing oil in the form of emulsion, a separation may often be effected by agitation with ether. For the extraction of unsaponifiable matter Förster has devised an apparatus which is figured and described in Vol. 1, page 82.

Purification of Oils.—The methods used in the refining and purification of crude oils have often considerable influence upon the analytical characteristics of the final products.

Action of Heat.—Simple application of heat may effect coagulation of protein impurities in an oil.

Mechanical Attraction and Filtration.—Substances such as Spanish clay, fuller's earth, and the like are used as mechanical precipitants of the suspended matter in oils. The clarified oil, which is not chemically altered by this treatment, is subsequently decanted or passed through a filter.

Treatment with Acids.—Rape, linseed, and some fish oils are frequently refined by treatment with a small proportion of sulphuric acid, which chars the impurities and causes them to subside without materially attacking the oil itself. The objection to the process is that traces of free mineral acid may remain, even after the subsequent washing with water, and, if the oil is used as a lubricant, may lead to corrosion of bearings, etc., or to charring of the wick in the case of lamp oils. Treatment with sulphuric or hydrochloric acid is also employed in the removal of the lime which is present in bone fat.

Treatment with Alkalies.—Certain oils, notably cottonseed, olive, and sperm oils, are frequently purified by treatment with a solution of caustic soda, the quantity of which depends upon the amount of free fatty acids and impurities to be removed. Cottonseed oil contains a notable proportion of a resin-like substance which gives a blue coloration with the alkali. Ammonia, sodium carbonate, magnesium carbonate, milk of lime, and sodium peroxide are also employed in certain refining processes. Oils, which have been treated with alkali usually contain a much smaller amount of free fatty acids than even the freshly-expressed crude oils, and cottonseed oil used for cooking purposes is often practically neutral.

Treatment with Oxidising Agents.—Fish oils are purified, and to some extent deodourised, by treatment with a current of steam followed by a current of hot air. Excessive treatment of this kind will alter the character of the oil itself, so that it becomes heavier and more viscous, and acquires other characteristics of "oxidised" or "blown" oils (*q. v*). Palm oil is bleached by hot air in a similar fashion. Of chemical oxidising reagents mention may be made of dichromate and mineral acid (used in the purification of palm oil), manganese dioxide and hydrochloric acid, and hydrogen peroxide. Wax bleached by chlorine is apt to contain chlorine fatty compounds, which are decomposed with the liberation of hydrochloric acid when the wax is subsequently burnt in the form of candles.

Chemical Precipitants.—Protein impurities in fish oils and other oils may be chemically precipitated by means of tannin or solutions of metallic salts capable of combining with them.

For details of these and similar methods of clarifying, bleaching, and deodorising oils see Alder Wright and Mitchell's, *Oils, Fats, and Waxes*, 1903, 310.

Purification by Pressure.—Hydraulic pressure is widely employed for separating the solid from the liquid constituents of oils. The solid fats thus separated are commercially known as "stearin," though, as a rule, they are far from approximating in composition to the triglyceride of stearic acid. Similarly, the liquid expressed oils are conveniently termed "oleins," though of very complex composition. The following are some of the chief instances in which commercial fats and oils are separated by pressure into solid and liquid portions.

Original oil	Liquid product	Solid product
Olive oil.	Purified olive oil.	Olive oil stearin.
Cottonseed oil.	Purified cotton oil.	Cotton oil stearin.
Coconut oil.	Coconut olein.	Coconut stearin.
Tallow.	Tallow oil.	Tallow stearin.
Lard.	Lard oil.	Lard stearin.
Whale oil.	Purified whale oil.	Whale stearin.
Sperm oil.	Purified sperm oil.	Spermaceti.

CONSTITUTION AND CHEMICAL PROPERTIES OF FATS, OILS, AND WAXES.

The fats, fixed oils, and waxes are esters of a series of acids mostly monobasic and called, from their sources, the fatty acids. The natural fats and fixed oils are all esters of the triad radicle, $.CH_2.CH.CH_2$. Their composition may be expressed by the general formula $C_3H_5A_3$, in which A is a radicle of some acid. From the fact that the radicle

C_3H_5 occurs in glycerol, it is generally called *glyceryl* or *glycyl*, and the esters are usually called *glycerides*.

The fatty acids most commonly forming esters with the glyceryl radicle in natural fats and oils are those belonging to the series with the general formulæ, $C_nH_{2n}O_2$ (acetic or stearic acid series); $C_nH_{2n-2}O_2$ (oleic acid series); $C_nH_{2n-4}O_2$ (linolic acid series); $C_nH_{2n-6}O_2$ (linolenic acid series), and $C_nH_{2n-2}O_3$ (ricinoleic or hydroxyacrylic acid series).

Glyceryl stearate, $C_3H_5(C_{18}H_{35}O_2)_3 = C_{57}H_{110}O_6$, is known as tristearin, or stearin; it is probably the chief constituent of beef and mutton tallow. In like manner olein is probably the principal component of almond, olive, and lard oils, and palmitin of palm oil. Esters of linolic acid are main constituents of cottonseed and maize oils, while the esters of linolenic and isolinolenic acid form an important part of linseed oil, and that of ricinoleic acid of castor oil. Olein, linolein, and linolenin, being liquid, predominate in oils, while stearin and palmitin are more abundant in solid fats.

The view formerly held that the natural esters rarely contain more than one acid radicle requires modification, since it has been shown that *mixed glycerides*, in which the acid radicles are not all of the same kind, are present in numerous fats. Thus Heise (*Arbeit a. d. Kaiserl. Gesundheitsamt*, 1896, 540) and subsequently Henriques and Künne (*Ber.*, 1899, **32**, 387) isolated oleo-distearin from the fat of the seeds of the East African tallow tree (*Stearodendron Stuhllmanni*), and the bromides of mixed glycerides were separated by Hehner and Mitchell (*Analyst*, 1898, **23**, 317) from linseed oil, walnut oil, and marine animal oils. The separation and behaviour of these bromides is a valuable test for distinguishing between different classes of oils, as is shown in a subsequent section.

The waxes proper contain the esters of higher alcohols of the methyl series. Thus spermaceti consists chiefly of cetyl palmitate, $C_{16}H_{33}$-$C_{16}H_{31}O_2$, whilst Chinese wax, beeswax, and carnaüba wax contain still higher radicles. Sperm oil and bottlenose oil are chiefly composed of substances having a constitution similar to that of the waxes.

In addition to the esters which constitute the essential portions, most natural fats, oils, and waxes contain more or less of free fatty acids, and small proportions of colouring, odorous, resinous, and other matters, to which the characteristic colours, smells, and tastes are mostly due. Small proportions of cholesterols or phytosterols are also present, and their separation affords a means of distinguishing between oils of animal and of vegetable origin.

Free fatty acids in natural fats and oils are usually products of decomposition, accelerated by the presence of mucilaginous or protein matters. Ordinary butter, which contains casein, readily turns rancid and then contains free butyric acid; but if all casein and water are removed by melting and filtering the butter, the butter-fat may be kept unchanged for a much longer time. Over-treatment with sulphuric acid in the process of refining oils often results in the formation of free fatty acids. Commercial oils which have been refined by this process are apt to retain traces of free mineral acid.

Acid Value.—The proportion of free fatty acids is best ascertained by shaking a weighed quantity of the fat with warm alcohol and titrating the solution with a standard alkali solution, with phenolphthalein as indicator.

An accurately weighed quantity of the sample, ranging from 5 grm. of fatty acid to 50 grm. of an ordinary oil, is introduced into a flask or bottle furnished with a glass stopper, and from 50 to 100 c.c. of pure neutralised alcohol containing a little phenolphthalein in solution is added and raised to the boiling-point by immersing the bottle in hot water. The contents are thoroughly agitated to effect as complete a solution of the fatty acids as possible. If the sample of oil is wholly free from acid, the pink colour of the alcohol will remain unchanged, but otherwise it will disappear. In the latter case, a N/2 solution of sodium hydroxide is added in small amounts to the warm contents of the flask, which is shaken thoroughly after each addition until the pink colouration persists. The reaction is as well defined and the neutralisation point as easy to perceive as in the titration of mineral acids; but owing to the very high combining weights of the fatty acids, great care is necessary. Thus 1 c.c. of N/2 alkali used corresponds to 0.128 of *palmitic*, 0.142 of *stearic*, or 0.141 grm. of *oleic acid*. For determining small proportions of free acid, it is desirable to employ decinormal alkali, while in the case of samples containing much free acid the quantity taken for the assay should be correspondingly reduced. The result is usually expressed in terms of the number of mg. of potassium hydroxide neutralised by 1 grm. of the fat, and is termed the *Acid Value*.

If the mean equivalent weight of the free fatty acids be known, their percentage may readily be calculated from the acid value. For this purpose it is often assumed that the free fatty acids in oils consist solely of oleic acid, and since 282 parts of oleic acid are equivalent to 56.1 parts of potassium hydroxide, the percentage of free fatty acids (expressed as oleic acid) is obtained by multiplying the acid value by the factor 0.502.

The amount of free fatty acids in commercial oils is often very considerable. Thus in palm oil the free acid, calculated as palmitic acid, usually ranges from 12 to nearly 80%. In 89 samples of olive oil intended for lubricating use, Archbutt (*Analyst*, 1884, **9**, 171) found from 2.2 to 25.1 of free (oleic) acid, the mean being 8.05%. In the superior grades of olive oil the proportion of free acid is much smaller. In rape oil the percentage of free acid is generally from 1.5 to 6%; but cottonseed oil, which is refined by means of alkali, is generally free from any trace of acid.

The influence of free acid in an oil upon its tendency to act upon metals is considered in the section on "Lubricating Oils."

In the case of fats of a dark colour sharper readings may be obtained by the use of the indicator, known as *Alkali blue* 6 B (red with alkalies) in place of phenolphthalein. About 2 c.c. of a 2% alcoholic solution are added.

In determining the acid value of artificially coloured fats the dyestuff must, if possible, be removed before the titration by treatment with a suitable solvent, such as 80% alcohol or petroleum spirit, which in some cases dissolves the fat and leaves the dyestuff (*e. g.*, nigrosine in leather fats). Sometimes the dyestuff may be removed by shaking an ethereal solution of the fat with dilute hydrochloric acid, and washing the residual fat solution with water. Or the petroleum spirit solution of the fat may be thoroughly shaken with a measured quantity of N/10 alcoholic sodium hydroxide solution, and the aqueous layer subsequently titrated with standard hydrochloric acid until colourless to phenolphthalein.

Saponification of Fixed Oils.—*Fatty oils* heated with water under a pressure of 8 to 12 atmospheres or distilled with superheated steam are hydrolysed into fatty acids and glycerol. This method of decomposing fats is employed in the industrial production of fatty acids and glycerol.

Many natural oils and fats are partially hydrolysed into fatty acids and glycerol probably by the action of air and light and possibly bacterial action in presence of traces of albuminous or other foreign matter. The free fatty acids often present in commercial palm oil, olive oil, and tallow are due to this cause.

The lipoclastic enzymes present in castor and other oil seeds are also capable of effecting the hydrolysis of fats in the presence of dilute acid and water, as was shown by Connstein, Hoyer, and Wartenberg (*Ber.*, 1902, **35**, 3989).

Hydrolysis occurs when a fatty oil is heated to 110°, with about 8% of concentrated sulphuric acid. On washing the product with hot water, the sulphuric acid and glycerol are removed; and the fatty acids separate in the form of an oily layer.

An analogous action takes place when a fat or oil is treated with basic oxides or hydroxides. The change occurs more readily with some oils than with others, and is promoted by heat and by using alcohol or glycerol as a solvent for the alkali. A salt (soap) of the fatty acid is produced, glycerol being likewise formed. The soaps produced by potassium, sodium, or ammonium hydroxide are soluble in water, but most other soaps are insoluble.

Waxes yield soaps and a monatomic alcohol, instead of glycerol. The decomposition is usually difficult.

When an ester is split up into an acid and an alcohol, the change is usually called "saponification," no matter whether the agent effecting the change is water, an acid, or a base. The term is even extended to the decomposition of esters that do not yield fatty acids. It is evident, therefore, that the saponification of fixed oils is a definite chemical action, precisely analogous to the decomposition of the ordinary salts.

The table on page 12 gives the molecular weights and proportion of fatty acids and glycerol theoretically obtainable from pure triglycerides and other esters of common occurrence.

Hence it appears that the majority of fats and oils yield, on saponification, from 95 to 96% of fatty acids, and about 10% of glycerol. The esters of butyric, valeric, or lauric acid contained in butter-fat, porpoise, and coconut oils, respectively, yield a larger proportion of glycerol, while rape oil, containing an ester of erucic acid, yields a smaller proportion.

The waxes yield much smaller proportions of fatty acids, and, instead of glycerol, give large proportions of alcohols of the C_nH_{2n+1} series, as solid bodies insoluble in water. The nature and proportion of the products of saponification sharply distinguish sperm and bottlenose oils from all other fixed oils of commercial interest.

Esters	Chief sources	Formula	Molecular weight	Production of saponification of 100 parts	
				Fatty acid	Glycerol
Glycerides					
Tributyrin	Butter-fat	$C_3H_5(C_4H_7O_2)_3$	302	87.44	30.46
Trivalerin	Porpoise oil, whale oil.	$C_3H_5(C_5H_9O_2)_3$	344	88.96	26.77
Trilaurin	Coconut oil, palmnut oil	$C_3H_5(C_{12}H_{23}O_2)_3$	638	94.04	14.42
Tripalmitin	Palm oil, lard	$C_3H_5(C_{16}H_{31}O_2)_3$	806	95.28	11.41
Tristearin	Tallow, lard, cacao butter.	$C_3H_5(C_{18}H_{35}O_2)_3$	890	95.73	10.34
Triolein	Olive oil, almond oil, lard oil	$C_3H_5(C_{18}H_{33}O_2)_3$	884	95.70	10.40
Trierucin	Rape oil	$C_3H_5(C_{22}H_{43}O_2)_3$	1052	96.39	8.75
Trilinolin	Maize oil, cotton-seed oil	$C_3H_5(C_{18}H_{31}O_2)_3$	878	95.67	10.48
Triricinolein	Castor oil	$C_3H_5(C_{18}H_{33}O_3)_3$	932	95.92	9.88
Trilinolenin	Linseed oil and drying oils	$C_3H_5(C_{18}H_{29}O_2)_3$	872	95.64	10.55
					Mon-atomic alcohol.
Cetyl palmitate	Spermaceti	$C_{16}H_{33}.C_{16}H_{31}O_2$	480	53.33	50.42
Myricyl palmitate	Beeswax	$C_{30}H_{61}.C_{16}H_{31}O_2$	676	37.87	64.79
Ceryl cerotate	Chinese wax	$C_{27}H_{55}.C_{27}H_{53}O_2$	788	52.03	50.25
Dodecyl oleate	Sperm oil	$C_{12}H_{25}.C_{18}H_{33}O_2$	450	62.67	36.88
Dodecyl doeglate	Bottlenose oil	$C_{12}H_{25}.C_{19}H_{35}O_2$	464	63.79	35.78

The nature of the fatty acids produced on saponification is of importance in distinguishing the various fixed oils, as is shown in the description of their individual characteristics.

Theory of Saponification with Alkali.—Geitel (*J. pr. Chem.*, 1897, **163**, 429; 1898, **165**, 113) concluded from mathematical considerations that in the saponification of triglycerides with alkali, *diglycerides* and *monoglycerides* were formed as intermediate products. Thus where R represents a fatty acid radicle these stages may be represented:

Normal triglyceride	Diglyceride	Monoglyceride
$CH_2.OR$ | $CH.OR$ | $CH_2.OR$	$CH_2.OR$ | $CH.OR$ | $CH_2.OH$	$CH_2.OR$ | $CH.OH$ | $CH_2.OH$

This view was opposed by Henriques (*Zeit. angew. Chem.*, 1898, 697). Subsequently Lewkowitsch (*Ber.*, 1900, **32,** 89; 1906, **39,** 4095; *J. Soc. Chem. Ind.*, 1903, **22,** 596) has brought experimental evidence in support of Geitel's view, whilst the opposite view is maintained by Fanto (*Monatsh.*, 1904, **25,** 919; 1907, **28,** 383; *Annalen*, 1907, **351,** 532) and by Marcusson (*Ber.*, 1906, **39,** 3466). The question must still be regarded as unsettled.

In saponification with alcoholic alkali the ethyl esters of the different fatty acids in a fat are formed as intermediate products, and their separation by distillation affords a means of distinguishing between different oils and fats.

Alcoholysis of Fats.—When glycerides are subjected to the action of an alcohol containing a small quantity of an acid they are decomposed in a manner analogous to the hydrolysis effected by water in the presence of acid. A useful method of estimating the composition of fats has been based on this reaction by Haller (*Compt. rend.*, 1906, **143,** 657) who describes the process as "alcoholysis."

About 100 grm. of the dried fat are heated on the water-bath with 200 grm. of, *e. g.*, methyl alcohol, to which has been added 1 or 2% of dry hydrochloric acid, fresh additions of acidified methyl alcohol being made, if required, until the mixture appears homogeneous. It is then treated with a large volume of water or salt solution, which retains the excess of methyl alcohol and the glycerol from the fat, while the methyl esters of the fatty acids rise to the surface. These may then be separated by fractional distillation and the fatty acids in the distillates separated and identified. In the case of the methyl esters of butyric, caproic, and caprylic acids the distillation may be carried out at the ordinary temperature but from 194° (the b. p. of methyl caprylate) upward reduced pressure is necessary. The method gives good results up to lauric acid, but the separated esters of myristic, palmitic, and stearic acids always retain some methyl oleate. The latter may be separated by chilling the fractions with ice and draining the crystals on a porous tile with the aid of a pump.

By this method Haller and Youssoufian (*Compt. rend.*, 1906, **173,** 803) found coconut oil to contain caproic, caprylic, lauric, myristic, palmitic, stearic, and oleic acids; whilst Meyer (*Chem. Zeit.*, 1907, **31,** 793) found cottonseed oil to consist chiefly (up to 70%) of palmitin, with the glycerides of oleic, linolic, and probably stearic and arachidic acids.

Saponification in Analysis.—The most convenient method of saponifying oils, etc., for the further examination of their constituents is by treatment with an alcoholic solution of potassium hydroxide and subsequent evaporation of the alcohol:

An alcoholic solution of alkali is prepared by dissolving 80 grm. of potassium hydroxide in 1000 c.c. of strong alcohol, which has been previously redistilled with a little alkali. It is desirable to dehydrate the spirit by keeping it over a large excess of dry potassium carbonate. About 5 grm. of the clarified fat or oil are weighed in a 4-oz. wide-necked flask, treated with 25 to 30 c.c. of the solution of alkali in spirit, and the flask closed with a cork fitted with a long tube. The flask is heated over boiling water, and as soon as the spirit boils the contents are mixed by circular agitation. In most cases the whole of the oil will rapidly disappear, forming a clear solution of soap, which may be further heated for a short time with occasional agitation to ensure complete saponification of the fat. The cork is then removed and the alcohol evaporated. In the presence of unsaponifiable oil the contents of the flask should be allowed to boil until nearly dry, and the residue treated with 25 c.c. of spirit, and again boiled down. When there is no danger of loss of hydrocarbon oils or esters of lower fatty acids by incautious treatment, the saponification and subsequent evaporation may be satisfactorily conducted in a hemispherical porcelain basin, placed over a small naked flame. The mixture is well stirred with a glass rod, and kept gently boiling until the alcohol is nearly driven off and the residual liquid froths strongly. By this time the whole of the oil should have disappeared, but, if incomplete saponification is suspected, 10 c.c. of alcohol may be added, and the evaporation repeated.

To ensure the saponification of butter fat, codliver oil, the waxes, and other substances difficult to decompose, it is better to place the sample and alcoholic solution in a strong 200 c.c. bottle, closed by an India-rubber stopper firmly fastened by wire. The bottle is then kept at 100°, and frequently agitated during half an hour, or until no globules of oil can be seen, after which it is opened, and the contents rinsed into a basin and evaporated over boiling water till the alcohol is expelled. Special precautions for ensuring the saponification of waxes are described in the section on "Beeswax."

Saponification Values of Oils. *Koettstorfer's Process.*—The saponification of fatty oils being a perfectly definite reaction, not only can the proportions of fatty acid and glycerol produced from any particular ester be calculated, but the proportion of alkali required for the saponification can be similarly ascertained from the general equation: $C_3H_5\overline{A}+3KHO=C_3H_5(OH)_3+3K\overline{A}$. Conversely, if the proportion of alkali required to effect the saponification of a particular oil be accurately determined by experiment, the nature of the ester present can be inferred. From the above equation it appears that 1 molecule of a glyceryl ester requires 3 molecules of alkali for saponification. The number of parts saponified by 1 molecule of alkali will therefore be 1/3 of the molecular weight; but in the case of the ester of a monatomic alcohol, the number will be identical with the molecular weight. This figure, which really represents the number of grm. of an oil saponifiable by one equivalent in grm. of any alkali, or, in other words, the number of grm. of an oil which would be decomposed by 1,000 c.c. of a normal solution of any alkali, is conveniently designated the "saponification equivalent" of an oil, and may in all cases be found by dividing the percentage of potassium hydroxide required for saponification into 5610, or the percentage of sodium hydroxide into 4,000.

It is now customary, however, to express the results of this test in terms of the number of mg. of potassium hydroxide required for the complete saponification of 1 grm. of a fat or wax, this being known as the *saponification value.*

The estimation of the saponification value of an oil is best effected in the manner described by Koettstorfer (*Zeit. anal. Chem.*, 1879, **18**, 199), who applied it originally to the analysis of butter:

From 1.5 to 2 grm. of the sample, accurately weighed, are treated with 25 c.c. of approximately N/2 solution of potassium hydroxide in alcohol,[1] in a flask fitted with a long vertical tube. The flask is heated on the water-bath for about 1/2 hour, or until complete solution of the fat takes place, and the saponification is judged to be complete. The operation is greatly expedited by subjecting the contents of the flask to frequent agitation. 1 c.c. of 1 % alcoholic solution of phenolphthalein is then added, and the liquid titrated with N/2 hydrochloric acid; 25 c.c. of the potassium hydroxide solution, very carefully measured, should then be similarly treated without addition of fat, and titrated with hydrochloric acid in the same way as before.

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[1] The alcohol employed for making the solution should be previously dehydrated by keeping it over an excess of dry potassium carbonate. Methylated spirit may be used if it is first distilled with a little potassium hydroxide.

The difference between the volumes of standard acid used in the 2 estimations gives the number of c.c. corresponding to the alkali neutralised in saponifying the oil. Each c.c. of N/2 c.c. hydrochloric acid (=18.25 grm. HCl per 1000 c.c.) thus employed represents 0.02805 of KOH, whence the *number of mg. of potassium hydroxide* required to saponify 1 grm. of the oil can readily be ascertained.

The *saponification equivalent* of the oil is found by dividing the weight of the sample employed, expressed in mg., by the number of c.c. of N/1 (not N/2) acid corresponding to the alkali neutralised by the oil. If the percentage of potassium hydroxide required is known, the saponification equivalent can be found by dividing this percentage into 5610.

It is essential that the alcoholic alkali should be as free as possible from any colour, since any brown or yellow tint affects the sensitiveness of the acid reaction with phenolphthalein. The saponification and titration should be conducted with as little access of air as possible, since the action is influenced by the presence of carbonic acid.

It is absolutely necessary to ascertain the strength of the alcoholic alkali from day to day, as such solutions rapidly alter, and the mere heating is liable to cause a slight change in the neutralising power. Standard sulphuric acid cannot be conveniently substituted for the hydrochloric acid recommended for the titration, as its employment causes a precipitation of sulphate, which masks the end-point.

In the case of waxes the nature and amount of unsaponifiable matter renders saponification more difficult, and it is necessary to boil the substance for at least an hour over a flame protected by wire-gauze with an excess of 2N. alcoholic alkali prepared with alcohol of 96 to 98% strength. To prevent dissociation it is advisable to add. 20 c.c. of neutral alcohol to the liquid before titration.

Cold Saponification.—The method of cold saponification devised by Henriques (*Zeit. angew. Chem.*, 1891, 721) may sometimes be found of use for oils and fats, though it is not satisfactory in the case of waxes. From 3 to 4 grm. of the fat are dissolved in 25 c.c. of light petroleum and treated with 25 c.c. of N/1 alcoholic alkali solution, a blank estimation being simultaneously made. Both flasks are closed, shaken, and allowed to stand for 12 hours at the ordinary temperature, after which the excess of alkali is titrated with standard hydrochloric acid.

The following table gives the saponification values and saponification equivalents of the chief esters occurring as constituents of the natural fats and oils.

As already stated, the saponification-equivalents of the monatomic esters are identical with their molecular weights, while those of the glyceryl esters are one-third of their molecular weights.

Substance	Chief sources	Saponification value	Saponification equivalent
Butyrin	Butter-fat	557.3	100.67
Valerin	Porpoise, dolphin, and whale oils	489.2	114.67
Laurin	Coconut and palm-nut oils	263.8	212.67
Palmitin	Palm oil; lard	208.8	268.67
Stearin	Tallow; lard; cacao butter	189.1	296.67
Arachidin	Arachis oil	172.7	324.67
Olein	Olive, almond, and lard oils	190.4	294.67
Erucin	Rape oil	160.0	350.67
Linolin	Cottonseed, maize oils.	212.0	264.67
Linoleinin Isolinolenin	Linseed oil	191.7	292.67
Ricinolein	Castor oil	180.6	310.67
Cetyl palmitate	Spermaceti	116.9	480
Myricyl palmitate	Beeswax	83.0	676
Ceryl cerotate	Chinese wax	71.2	788
Dodecatyl oleate	Sperm oil	124.7	450
Dodecatyl doeglate	Bottlenose oil	120.9	464

Since the natural oils met with in practice do not consist of a single ester in a state even of approximate purity, the saponification values of ordinary oils and fats are the resultants of the values of their constituents, and therefore show less pronounced differences than do the pure esters.

Nevertheless, the peculiarity of constitution of many of the natural fats and oils is indicated by the results of this test. Thus rape oil and similar oils containing erucin have low saponification values, whilst, on the other hand, butter fat, containing butyrin and other glycerides of lower fatty acids gives high values.

The probable saponification values of oil and fats of commercial importance will be found in the tables on pp. 69–73. From the figures there given it will be seen that glyceridic oils and fats may be roughly classified into 3 groups in accordance with their saponification values: 1. Those with low values (169 to 181, usually about 175), such as castor oil and members of the rape-oil group. 2. Those with medium values (183 to 196), such as the majority of fats and oils; and 3. Those with high values due to the presence of lower fatty acids, such as members of the coconut-oil group, butter-fat, and certain marine-animal oils (group X). The waxes (Group XII) and sperm oil have exceptionally low saponification values indicative of their peculiar composition.

Since hydrocarbon oils do not interact with alkali the proportion of such oils in admixture with fatty oils may be deduced from the saponification value of the mixture. Thus if a sample of so-called linseed oil has a saponification value of only 9.5 instead of about 190, it may be assumed to contain approximately 95% of hydrocarbon oil.

Separation of the Products of Saponification.—The solution of soap, freed in the foregoing manner from alcohol, should then be diluted with warm water till it measures 70 to 80 c.c. A perfectly clear solution will usually be obtained if a pure oil has been used and the process has been successfully conducted, but *waxes* and mixtures containing *hydrocarbons* and other foreign matters will give a solution containing solid matter or oily globules in suspension. These admixtures may usually be removed and estimated by agitating the soap solution in a glass separator, with an immiscible solvent, ether being the most generally suitable for the purpose.[1] The ethereal layer is then separated, evaporated, and the residue weighed. The best method of manipulation is described later. Cholesterol and other unsaponifiable substances are present in small proportion, even in the purest fatty oils.[2]

If ether has been employed, it should be removed by keeping the soap solution at a gentle heat for some time. On then treating the solution with an acid, dilute sulphuric acid being generally preferable, a milky precipitate is produced, which, on warming the liquid, will collect into globules and form an oily layer on the surface. This layer consists of the *fatty acids* produced from the oil. These acids differ from the original esters in being soluble in alcohol, the solution having an acid reaction, and decomposing the carbonates of the alkali metals, liberating carbon dioxide and forming soaps.

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[1] Owing to the limited solubility of myricyl alcohol in most solvents, the method described in the text is attended with practical difficulties in the case of beeswax and carnaüba wax, though it is admirably adapted for the analysis of spermaceti. If the removal of the separated higher alcohol by an immiscible solvent be found impracticable, the solution of the soap should be treated with acetic acid in quantity just sufficient to destroy the pink coloration produced by phenolphthalein, and the solution treated with lead acetate. The precipitate should be washed, dried, mixed with sand, and the wax-alcohol dissolved in boiling petroleum spirit.

[2] In rigidly accurate experiments it is desirable to treat the unsaponified residue in the same manner as the original oil, as traces of fat are liable to escape saponification by a single treatment. If the residue left on evaporating the ethereal solution be treated with a little hot alcohol, the solution filtered hot, and the filtrate cooled, and, if necessary, allowed to evaporate spontaneously, crystalline plates of cholesterol will often be deposited.

The higher fatty acids are almost wholly insoluble in water and not sensibly volatile at 100°, but from butter-fat, coconut oil, palmnut oil, porpoise oil, and some others a notable amount of the lower fatty acids is obtained, and hence the acids from these sources are partially soluble in water and capable of distillation with water at 100°.

For obtaining these *soluble* or *volatile acids* from oils, the soap solution is acidified with sulphuric acid in the manner already described, the aqueous liquid separated from the layer of fatty acids, and the latter boiled several times with a considerable quantity of water in a flask furnished with a long tube or inverted condenser. The liquids resulting from these operations are separated from the *insoluble fatty acids*, which it is desirable to boil again with a moderate quantity of water, whilst driving a current of steam through the flask in which they are contained, collecting the distillate, and treating it like the washings.[1] The acidified aqueous liquid first separated from the layer of fatty acids is then distilled to small bulk and the distillate exactly neutralised with a standard solution of sodium or barium hydroxide, using phenolphthalein as an indicator. The first washings from the insoluble fatty acids are then added to the contents of the retort, and the liquid again distilled to a low bulk, the process being repeated with the succeeding washings. The different distillates obtained should be titrated separately with N/10 standard alkali and phenolphthalein, as, in this manner, with but little extra trouble, the progress and completion of the washing, etc., can be followed, and useful information obtained as to the probable nature and relative proportions of the *lower fatty acids* present.

The several neutralised distillates may now be united and evaporated gently to dryness, the residue being dried at 100° till constant in weight. It consists of the sodium or barium salts of the acids which passed over in the preceding distillation. If the total volume (in c.c.) of N/1 sodium hydroxide solution employed for the neutralisation be multiplied by 0.022, or the volume of N/1 barium hydroxide solution by 0.0675, and the number so obtained be subtracted from the gross weight (in grm.) of the dry residue, the difference will be the weight of the *volatile fatty acids*. Their mean combining equivalent will be found by dividing their weight by the volume (in c.c.) of normal alkali required for their neutralisation.

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[1] When coconut or palm-nut oil is treated in this manner, the distillate will be found to contain lauric acid, which, though almost insoluble in water, is volatile in a current of steam. It may be separated from the more soluble volatile fatty acids by filtering the distillate.

A further examination of the volatile fatty acids can be made by distilling the barium or sodium salts with phosphoric or diluted sulphuric acid, and examining the distillate as indicated in Vol. 1, p. 235. In Reichert's method (see below) an aliquot portion of the acidified solution of the saponified fat is distilled, and the distillate titrated with standard alkali.

Hehner Value.—In cases in which the oil under examination is known not to contain any appreciable quantity of esters of the lower acids, the treatment for their isolation may be wholly omitted, and the *insoluble fatty acids* are then practically identical with the *total* fatty acids liberated on adding a dilute mineral acid to the aqueous solution of the soap. The oily layer thus obtained should be shaken several times with warm water, or until, after separation, the aqueous liquid is no longer acid to litmus. The subsequent treatment of the insoluble fatty acids will depend on the nature and extent of the information required. In some cases it will be sufficient to add alcohol and titrate with standard alkali with phenolphthalein as indicator.

If the fatty acids are to be weighed, the best mode of operating is to run them from the separator into a small paper filter previously wetted with hot water. The funnel containing the filter is placed in the mouth of a small dry beaker, and the whole heated in the water-oven. As the filter dries, the greater part of the fatty acids will pass through the paper into the beaker. When no more drops through, the funnel is removed to a small dry flask, and the acids adhering to the separator or other vessels removed by means of ether, carbon tetrachloride, or petroleum spirit. The solution thus obtained is poured into the filter and caught in the flask below. A fresh quantity of the solvent is used to effect complete solution and removal of the fatty acids from the filter, these washings also being allowed to run into the flask. The solvent is then distilled off by immersing the flask in hot water, and the residual fatty acids further dried by blowing a current of air through the flask till they begin to lose weight, or till all odour of the solvent has disappeared. The weight of fatty acids thus estimated is added to that of the main quantity contained in the beaker, and the sum gives the *insoluble fatty acids* in the amount of fat employed for the analysis.

The result expressed in percentage of the fat is commonly termed the *Hehner value*. It usually ranges from about 95.5 to 96% in the case of fats containing only minute quantities of soluble fatty acids.

In most cases the estimation of the *total* insoluble fatty acids is sufficient, but, if desired, a further proximate analysis may be made by the methods indicated in the section on "Higher Fatty Acids."

The acidified aqueous liquid remaining after the isolation of the insoluble fatty acids, and the removal of any volatile fatty acids by distillation, contains *glycerol*, which may be isolated by exactly neutralising the free acid with potassium hydroxide, evaporating the solution to dryness on the water-bath, and exhausting the residue with alcohol. On filtering and evaporating the alcoholic solution, the glycerol is obtained as a sweet syrupy liquid, which may be further purified by treatment with a mixture of alcohol and ether and evaporation of the filtered solution. Although glycerol resulting from the saponification of oils may be readily isolated in this manner, the results obtained are only very roughly quantitative, owing to loss during the evaporations. The estimation of the glycerol produced by saponification is most accurately effected by the methods described in the section on "Glycerol."

The following table shows in a condensed form the general process, just described, for the separation of the products of saponification of genuine fixed oils. The method of estimating *foreign additions* to fixed oils is described in a separate section.

<table>
<tr><td colspan="5">Saponify the oil, evaporate off the alcohol, dissolve the residual soap in water, and agitate the solution with ether.</td></tr>
<tr><td rowspan="3">Ethereal Solution contains <i>cholesterol, phytosterol, hydrocarbons, unsaponified oil, and higher alcohols</i> (from waxes, sperm oil, etc.).</td><td colspan="4">Aqueous Layer. Acidify with dilute sulphuric acid, and wash liberated fatty acids with boiling hot water.</td></tr>
<tr><td colspan="2">Oily Layer consists of <i>insoluble fatty acids</i>, which may be converted into lead salts and partially separated by treatment with ether.</td><td colspan="2">Aqueous Liquid on distillation gives—</td></tr>
<tr><td>More Soluble in Ether. Lead compounds of <i>oleic, ricinolic, linolic, linolenic, hypogeic acids, etc.</i></td><td>More Insoluble in Ether. Lead compounds of <i>myristic, palmitic, stearic, arachidic, cerotic acids, etc.</i></td><td>In Distillate <i>lower fatty acids</i>, such as <i>butyric, valeric, caproic, lauric, etc.</i>; estimated by titration with standard alkali, and further examined by fractional distillation, etc.</td><td>In Retort, an aqueous liquid, which, when neutralised, carefully evaporated to dryness, and the residue treated with ether-alcohol, gives a solution of <i>glycerol</i>, left as a sweet syrupy liquid on evaporating the solvent, but which is more accurately <i>estimated</i> in a separate portion by oxidation.</td></tr>
</table>

Reichert Value.—This term is applied to the number of c.c. of N/10 alkali solution required to neutralise the distillate obtained from the acidified solution of a fat saponified under definite empirical conditions. It was devised by Reichert (*Zeit. anal. Chem.*, 1879, **18,** 68), and, though practically superseded by later modifications, is still used in some laboratories, and is the method by which the earlier recorded values were obtained.

As the process is an arbitrary one, only about 4/5 of the entire volatile fatty acids obtainable from butter being found in the distillate under the conditions of operation, it is necessary to adhere to the following directions: Saponify 2.5 grm. of the fat with 25 c.c. of approximately N/2 alcoholic potassium hydroxide, by heating it in a closed bottle or flask fitted with a long tube. Transfer the product to a porcelain basin, and evaporate off the alcohol *completely* at a steam heat. Dissolve the residual soap in water, add dilute sulphuric acid in slight excess, dilute the liquid with water to 75 c.c., add some fragments of pumice coiled round with platinum wire, and distil gently till 50 c.c. have passed over. Filter the distillate, if not quite free from white flakes or oily globules, wash the filter with a little hot water, and titrate the clear solution with N/10 alkali, using phenolphthalein as an indicator.

The following table gives typical Reichert values thus obtained:—

Substance	Cubic centimetres of $\frac{N}{10}$ alkali required	Observer
Butter- or milk-fat, cow's	12.5–15.2	Reichert, Caldwell, Moore, Allen, etc.
Butter- or milk-fat, ewe's	13.7	Schmitt.
Butter- or milk-fat, goat's	13.6	Schmitt.
Butter- or milk-fat, porpoise's	11.3	Allen.
Coconut oil	3.5–3.7	Reichert, Moore, Allen.
Palmnut oil	2.4	Allen.
Palm oil	0.8	Moore.
Cacao butter	1.6	Moore.
Margarine	0.2–1.6	Caldwell, Moore, Allen.
Whale oil	3.7	Allen.
Whale oil	12.5	Allen.
Porpoise oil	11–12	Allen.
Sperm oil	1.3	Allen.
Bottlenose oil	1.4	Allen.
Menhaden oil	1.2	Allen.
Codliver oil	1.1–2.1	Allen.
Sesame oil	2.2	Allen.
Cottonseed oil	0.3	Moore.
Castor oil	1.4	Allen.

Reichert-Meissl Value.—In Meissl's modification of Reichert's process (*Dingler's Polyt. J.*, 1879, **233**, 229) double the quantity of fat (5 grm.) is used, and the resulting values are about 2.2 times as great. His modification is in common use, with the additional precautions indicated by Wollny (*Analyst*, 1887, **12**, 203, from *Milch Zeit.*, 1887, Nos. 32–35) to ensure complete saponification of the fat, and to obviate errors due to absorption of carbon dioxide, and variations in the form and size of the distillation apparatus and the rate of distillation.

The special form of apparatus and method of distillation official in this country is described in the section dealing with "*Butter.*"

The following official process of the A. O. A. C. is essentially the method as recommended by Wollny:

Apparatus and Reagents.

Sodium Hydroxide Solution.—100 grm. of sodium hydroxide are dissolved in 100 c.c. of distilled water. The sodium hydroxide should be as free as possible from carbonates, and be preserved out of contact with the air.

Alcohol, of about 95%, redistilled with sodium hydroxide.

Acid.—Solution of sulphuric acid containing 25 c.c. of strongest sulphuric acid in 1,000 c.c. of water.

Barium Hydroxide.—An accurately standardised, approximately N/10 solution of barium hydroxide.

Indicator.—1 grm. of phenolphthaleïn in 100 c.c. of alcohol.

Saponification flasks, of from 250 to 300 c.c. capacity, of hard, well-annealed glass, capable of resisting the tension of alcohol vapor at 100°.

Pipette graduated to deliver 40 c.c.

Distilling Apparatus

Burette.—An accurately calibrated burette, reading to tenths of a c.c.

Estimation.—*Weighing the fat.*—The butter or fat to be examined should be melted and kept in a dry, warm place, at about 60° for 2 or 3 hours, until the water and curd have entirely settled out. The clear, supernatant fat is poured off and filtered through a dry filter-paper in a jacketed funnel containing boiling water. Should the filtered fat, in a fused state, not be perfectly clear, it must be filtered a second time.

The saponification flasks are prepared by thoroughly washing with water, alcohol, and ether, wiping perfectly dry on the outside, and heating for 1 hour at the temperature of boiling water. The flasks should then be placed in a tray by the side of the balance and covered with a silk handkerchief until they are perfectly cool. They must not be wiped with a silk handkerchief within 15 or 20 minutes of the time they are weighed. The weight of the flasks having been accurately determined, they are charged with the melted fat in the following way:

The pipette with a long stem, marked to deliver 5.75 c.c., is warmed to a temperature of about 50°. The fat, having been poured back and forth once or twice into a dry beaker in order to mix it thoroughly, is taken up in the pipette, and 5.75 c.c. of fat allowed to flow into the flask. After the flasks have been charged in this way they should be re-covered with the silk handkerchief and allowed to stand 15 or 20 minutes, when they are again weighed.

Saponification.—10 c.c. of 95% alcohol are added to the fat in the flask, and then 2 c.c. of sodium hydroxide solution. A soft cork stopper is now inserted in the flask and tied down with a piece of twine. The saponification is then completed by placing the flask upon the water- or steam-bath. During the saponification, which should last 1 hour, the flask should be gently rotated from time to time, care being taken not to project the soap for any distance up its sides. At the end of an hour the flask, after having been cooled to about the temperature of the room, is opened.

Removal of the Alcohol.—The stopper having been laid loosely in the mouth of the flask, the alcohol is removed by dipping the flask into a steam-bath. The steam should cover the whole of the flask except the neck. After the alcohol is nearly removed, frothing may be noticed in the soap, and, to avoid any loss from this cause or creeping of the soap up the sides of the glass, the flask should be removed from the bath and shaken to and fro until the frothing disappears. The last traces of alcohol vapor may be removed from the flask by waving it briskly, mouth down, to and fro.

Dissolving the Soap.—After the removal of the alcohol the soap should be dissolved by adding 100 c.c. of recently-boiled distilled water, and warming the flask on the steam-bath with occasional shaking until solution of the soap is complete.

Liberation of the Fatty Acids.—When the soap solution has cooled to about 60° or 70°, the fatty acids are separated by adding 40 c.c. of the dilute sulphuric acid solution.

Melting the Fatty-Acid Emulsion.—The flask should now be stoppered as in the first instance, and the fatty-acid emulsion melted by replacing the flask on the steam-bath. The time required for the fusion may vary from a few minutes to several hours, according to the nature of the fat examined.

Distillation.—After the fatty acids are completely melted, forming a transparent oily layer on the surface of the water, the flask is cooled to the temperature of the room, and a few pieces of pumice-stone added. The pumice-stone is prepared by throwing it, at a white heat, into distilled water, and keeping it under water until used. The flask is now connected with a glass condenser, slowly heated with a naked flame until ebullition begins, and then the distillation continued by regulating the flame in such a way as to collect 110 c.c. of the distillate in, as nearly as possible, 30 minutes. The distillate should be received in a flask accurately marked at 110 c.c.

Titration of the Volatile Acids.—The 110 c.c. of distillate, after thorough mixing, are filtered through perfectly dry filter-paper, 100 c.c. of the filtrate poured into a beaker holding from 200 to 250 c.c., 0.5 c.c. of the phenolphthaleïn solution added, and N/10 barium hydroxide run in until a red colour is produced. The contents of the beaker are then returned to the measuring flask to remove any acid remaining therein, poured again into the beaker, and the titration continued until the red colour produced remains apparently, unchanged for 2 or 3 minutes. The number of c.c. of N/10 barium hydroxide required should be increased by one-tenth.

Leffmann and Beam's modification (*Analyst*, 1891, **16**, 153; 1896, **21**, 251) in which a solution of sodium hydroxide in glycerol is used for the saponification is the official German method for the examination of fats and cheese, the estimation being made as follows: 5 grm. of the fat are cautiously heated with constant shaking over a small flame in a 300 c.c. Erlenmeyer flask with 20 c.c. of glycerol of sp. gr. 1.26, and 2 c.c. of sodium hydroxide solution (prepared by dissolving 100 grm. of sodium hydroxide in 100 c.c. of water). After evaporation of the water, which usually takes from 5 to 8 minutes, the liquid becomes clear, and is then completely saponified. It is now allowed to cool to about 80°, and treated with 90 c.c. of water at 80° to 90°. This solution is acidified with 50 c.c. of dilute sulphuric acid (50 c.c. of strong acid in 1,000 c.c. of water) and the volatile fatty acids distilled and titrated as in the Reichert-Meissl process.

The following typical Reichert-Meissl values have been recorded by different observers:

Oil or fat	Reichert-Meissl value	Oil or fat	Reichert-Meissl value
Almond	0.5	Maize oil	4 to 4.5
Arachis	0.5	Palmnut oil	5 to 6.8
Butter fat	21.0–33.4.	Porpoise oil	0.8 to 1.9
Castor	2.5	Palm oil	0.0 to 0.7
Croton	12–13.5.	Rape	46 to 56
Cottonseed	0.7–0.9	Sesame oil	1 to 2
Coconut oil	6.6–8.4	Whale oil	0.7 to 2.0
Codliver oil	0.2	Wheat oil	2 to 3
Doegling oil	1.4		
Dolphin oil	5–6		

BROMINE AND IODINE ABSORPTIONS.

Another method of differentiation based on the chemical constitution of the fats and oils is the estimation of the amount of bromine or iodine taken up under conditions intended to ensure the formation of additive compounds only. The fatty acids of the acetic series are saturated bodies, and do not form additive compounds with iodine or bromine, while the acids of the acrylic series combine with 2 atoms and those of the propiolic series with four atoms, as expressed by the following equations:

Stearic Acid, $C_{18}H_{36}O_2$, does not combine with bromine or iodine.
Oleic Acid, $C_{18}H_{34}O_2$, forms $C_{18}H_{34}Br_2O_2$, and $C_{18}H_{34}I_2O_2$.
Linolic Acid, $C_{18}H_{32}O_2$, forms $C_{18}H_{32}Br_4O_2$, and $C_{18}H_{32}I_4O_2$.
Linolenic Acid, $C_{18}H_{30}O_2$, forms $C_{18}H_{30}Br_6O_2$, and $C_{18}H_{30}I_6O_2$.

The esters of the acids of these series behave similarly, so that an estimation of the percentage of bromine or iodine assimilated gives some idea of the proportion of olein as compared with palmitin and stearin in a fat, and of the linolin and linolenin of a drying oil as compared with the olein of a non-drying oil, although the fact must not be lost sight of that many solid fats contain esters of linolic and even linolenic acid, whilst drying oils contain olein in addition to the more unsaturated glycerides.

Bromine Value.—The earliest methods of estimating the amount of bromine absorbed by oils and fats were those of Mills and

Snodgrass (*J. Soc. Chem. Ind.*, 1883, **2**, 435) and Mills and Akitt (*ibid.*, 1884, **3**, 366), but for most purposes these and similar methods have now been practically superseded by Hübl's iodine method and Wijs' iodine chloride method.

A considerable amount of bromine enters into combination by way of substitution as well as by addition, and McIlhiney (*J. Amer. Chem. Soc.*, 1894, **16**, 275; 1899, **21**, 1084) has based a useful test for the detection of rosin or turpentine in drying oils upon a determination of the *bromine substitution value.*

The solution of the weighed quantity of the oil in 10 c.c. of carbon tetrachloride is treated in a stoppered bottle with 20 c.c .of 1/3 N. solution of bromine in the same solvent. After the lapse of 2 or 3 minutes 20 to 30 c.c. of a 10% solution of potassium iodide are introduced, the bottle thoroughly shaken, and the liberated iodine titrated with standard thiosulphate solution, and calculated into the corresponding bromine addition value. An addition of 5 c.c. of a neutral 2% solution of potassium iodate is then made, and the liberated iodine, corresponding to the hydrobromic acid formed in the substitution, titrated and calculated into the bromine substitution value.

The loss of bromine or hydrobromic acid is prevented by fixing a piece of wide india-rubber tubing round the neck of the bottle, so as to form a well into which the potassium iodide solution is poured. The bottle is then cooled in ice-water to create a partial vacuum before slightly withdrawing the stopper.

The bromine substitution value of ordinary fats and oils usually ranges from about 0.3 to 3.6, whilst rosin and turpentine show values of 50 and upward.

Vulté and Logan (*J. Amer. Chem. Soc.*, 1901, **23**, 156) made comparative estimations of the bromine value by this method and of the iodine value by Hübl's method, and showed that the ratio between the iodine value as estimated and as calculated from the bromine addition value might afford useful indications in the detection of marine animal oils in linseed oil, etc. They found rosin to have a bromine substitution value of 102.3.

Comparative results obtained by Wijs' iodine chloride method and McIlhiney's bromine method are also given by Williams (*J. Soc. Chem. Ind.*, 1900, **19**, 300). A gravimetric bromine method was devised by Hehner (*Analyst*, 1895, **20**, 49, *J. Soc. Chem. Ind.*, 1897, **16**, 88)) and was discussed by Lewkowitsch (*J. Soc. Chem. Ind.*, 1896, **15**, 859), Williams (*Analyst*, 1895, **20**, 277), and Jenkins (*J. Soc. Chem. Ind.*, 1897, **16**, 193).

The main advantages of this method, where applicable, are its simplicity and speed, but both are possessed in greater degree by the bromine thermal process (*q. v.*)

Insoluble Bromide Test.—Hehner and Mitchell found (*Analyst*, 1898, **23**, 315) that on treating an ethereal solution of certain oils with a slight excess of bromine an insoluble precipitate was obtained, the amount of which could frequently give valuable indications as to the purity of an oil.

These precipitates appear to be the bromides of mixed glycerides containing one radicle of linolenic acid or (in the case of marine animal oils) the isomeric jecoric acid. The bromide from linseed oil melts at 143.5 to 144° and contains about 56% of bromine. The similar bromides from marine animal oils decompose before melting, and this affords a means of detecting even a small amount of such oils in linseed and other drying oils.

The precipitate may be collected either in a Soxhlet tube, if the quantity taken is small, or on a counterpoised filter, but the method employed for the estimation of stearic acid in mixtures of fatty acids (see page 393); is the most satisfactory, the best filtering material in this case being thin, flexible chamois leather tied over the end of the small thistle funnel, from which any adhering precipitate can afterwards readily be removed by washing.

From 1 to 2 grm. of the sample are dissolved in 40 c.c. of ether, to which a few c.c. of glacial acetic acid are added, the precipitate formed being more granular from such a mixture than when ether alone is employed. The solution is cooled in an ice-chest and bromine added, the flask being preferably left all night in the ice. This, however, is not essential for ordinary working. The liquid is filtered off by the suction funnel attached to a pump, the flask washed out with four successive portions of ether at 0°, and the residue dried in the flask to constant weight. Even when ether at ordinary temperatures is used, no considerable error is introduced.

Various samples of pure linseed oil were examined by this method, with the following results:

Sample	Oil taken	Weight precipitate	Percentage of deposit
A	1.3226	0.3156	23.86
A	3.1005	0.7573	24.42
B	0.6792	0.1765	25.8
C	1.0000	0.2480	24.8
C	1.0000	0.2500	25.0

A sample of walnut oil gave, in two determinations, 1.9 and 1.42% of bromide. Poppy oil gave no deposit, nor did Brazil nut oil, maize oil, cottonseed oil, olive oil, Japanese wood oil, or almond oil. Mixtures of linseed oil and other oils gave percentages of bromide in proportion to the percentage of linseed oil, as will be seen from the following table:

Oils used	Linseed oil, %	Insoluble bromide, %	Linseed oil, calculated from bromide %
Linseed A and walnut	69.0	16.6	69.0
Linseed A and walnut	38.2	9.3	38.1
Linseed A and maize oil	52.0	12.4	50.8
Linseed A and maize oil	50.5	12.2	50.0
Linseed A and maize oil	51.7	12.6	51.6

The following values were obtained in this way by Walker and Warburton (*Analyst*, 1902, **28**, 237): Linseed oil, 23.14; 23.52; tung oil, nil; candlenut oil, 8.2; 7.28; Japan fish oil, 21.14; 22.07; fish oil (deodorised) 49.0; 52.28; codliver oil, 35.33; 33.76; cod oil, 32.68; 30.62; shark-liver oil, 21.22; 19.08; seal oil, 27.54; 27.92; whale oil, 15.54; 16.14; and sperm oil, 2.61; 2.42% (and after 48 hours' standing, 3.72; 3.69).

As a rule linseed oil yields about 25% of insoluble bromide, but Mitchell has met with a specimen yielding over 30% and Lewkowitsch with one giving 37.72%. Other insoluble bromide values for marine animal oils are given by Procter (*J. Soc. Chem. Ind.*, 1906, **25**, 798).

Iodine Value.—Free iodine is so slowly absorbed by oils and fats that it has not been found possible to base a satisfactory method upon its use, and it has long been discarded in favour of the Hübl process (*Dingler's polyt. J.*, 1884, **253**, 281) in which the reagent is an alcoholic solution of iodine in conjunction with mercuric chloride in the proportion of at least 1 molecule (I_2) of the former to at least 1 ($HgCl_2$) of the latter.

Hübl's Method.—The reagent is prepared by dissolving 25 grm. of iodine in 500 c.c. of nearly absolute alcohol (free from fusel oil), and 30 grm. of mercuric chloride in an equal measure of the same solvent. The latter solution is filtered, if necessary, and then added to the tincture of iodine. The mixed solution should be allowed to stand for 12 hours before being used, as, owing to the presence of impurities in the alcohol employed, it is liable to undergo considerable reduction in strength, and must in all cases be re-standardised immediately before or after use. The strength is ascertained by titration with decinormal solution of sodium thiosulphate, which in its turn is standardised by a solution of resublimed iodine in the usual way. The mercurial iodine solution acts readily at ordinary temperatures on either free unsaturated fatty acids or their esters to form chloro-iodo-addition products, the total proportion of halogen assimilated being estimated in terms of iodine.

To estimate the iodine-absorption, from 0.2 to 0.3 grm. of drying oil, 0.3 to 0.4 of non-drying oil, or from 0.8 to 1.0 grm. of fat, is weighed accurately, and dissolved in 10 c.c. of chloroform. The solution is mixed in a stoppered flask with 20 c.c. of the standard solution of iodo-mercuric chloride, and if the liquid is not quite clear after agitation a further addition of chloroform is made. If the mixture becomes decolorised, or nearly so, after standing a short time, a further addition of 5 or 10 c.c. of iodine solution must be made. To ensure accurate results, the excess of iodine must be considerable, and hence the liquid ought still to be quite brown after standing for 2 hours.[1] After that time, from 10 to 15 c.c. of a 10% aqueous solution of potassium iodide should be added, and the whole diluted with about 150 c.c. of water. The free iodine, part of which exists in the aqueous and part in the chloroform solution, is then estimated by titration with thiosulphate, the contents of the flask being frequently agitated, and starch solution being added just before the end of the reaction. A blank experiment with the same quantities of chloroform, iodine solution, etc., is made side by side with the actual test, so as to obtain a correction for any impurities in the reagents and to ascertain the true strength of the iodine solution. The difference between the volume of thiosulphate used in the blank experiment and that required in the experiment in which the oil was employed is then calculated into its equivalent of iodine, and this to units per cent. of the oil.

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[1] Hübl found that with free fatty acids the action is complete with only a small excess of iodine, but with fats or oils a larger excess must be employed, or the results will be too low. In presence of a sufficient excess of iodine, variations in the concentration of the fatty solution and in the amount of mercuric chloride present do not affect the results The reaction should be allowed to continue for at least 2 hours (or, according to Archbutt, 6 hours).

The product formed by the action of iodo-mercuric chloride on pure oleic acid is a greasy substance, which is colourless at first, but gradually turns brown from liberation of iodine. Estimations of the chlorine and iodine, as also of its saponification equivalent, show the compound to be a chloriodostearic acid of the formula $C_{18}H_{34}IClO_2$. The similar products formed by the action of the iodine solution on fats and oils are colourless, viscous, or resinous masses, which in general resemble the original substances. In order to render the whole of the iodine available, the presence of mercuric chloride in a ratio not less than $HgCl_2 : I_2$ is essential.

The theory of the reactions taking place in the Hübl process has been discussed by Ephraim (*Zeit. angew. Chem.*, 1895, 254), who regards iodine chloride as the active agent, by Wijs (*ibid.*, 1898, 251) who considers hypoiodous acid to be the active substance, and by Lewkowitsch (*Analyst*, 1899, **24**, 257) who in the main agrees with Ephraim. There is a certain amount of substitution of iodine as well as addition, as has been shown by Schweitzer and Lungwitz (*J. Soc. Chem. Ind.*, 1895, **14**, 130, 1030).

Wijs' Method.—A very rapid method of estimating the iodine absorption is based by Wijs (*Ber.*, 1898, **31**, 750) upon the conclusions drawn from his experiments (*loc. cit.*). The hypoiodous acid, which he regards as the active agent in the absorption, is obtained by the action of water upon iodine chloride ($ICl + H_2O = HCl + HIO$), a solvent being chosen which contains so much of the former as will decompose nearly the whole of the latter, and at the same time not be oxidised by the hypoiodous acid. Good results are obtained with a solution of iodine chloride in 95% acetic acid. This is prepared by dissolving 13 grm. of iodine in 1000 c.c. of acetic acid, estimating the "halogen content" of the solution and passing in a current of chlorine (free from hydrochloric acid) until the "halogen content" has been doubled. With a little practice this point is readily discernible by the change in colour. The solution is employed as Hübl's solution, except that the time required for absorption is greatly reduced. With oils of low iodine values, the absorption is complete in 4 minutes, and with those of higher value not more than 10 minutes will be necessary if too much oil is not taken.

The results obtained by Wijs' method tend to be higher than the Hübl figures, this being most notable in the case of highly unsaturated oils. It is probable that many of the older values of, *e. g.*, of linseed oil, were too low, owing to incomplete absorption of the halogen. The results obtained by Wijs with purified allyl alcohol point to his method giving more correct figures than the Hübl process.

In the following table the more common oils and fats are classified in accordance with their iodine values as estimated by various chemists by one or other of the preceding methods:

Oils	Iodine value	Fats and waxes	Iodine value
Vegetable oils		*Vegetable fats*	
Castor	84–85	Japan wax	4.2–15
Olive	77–91	Coconut oil	8.2–9.5
Arachis	86–99	Palmnut oil	10.5–17.5
Olive	77–91	Chinese tallow	23–38
Almond	93–100	Cacao butter	32–42
Rape	97–105	Bassia tallow	54–68
Sesame	103–115	Cotton oil "stearin"	89–93
Cottonseed	104–116		
Maize	115–128		
Nigerseed	126–134	*Animal fats*	
Sunflower	123–136		
Poppyseed	130–141	Tallow	35–40
Walnut	139–148	Beef fat	36–42
Hempseed	145–166	Mutton fat	33–50
Tung	155–162	Lard	47.5–64
Linseed	175–201	Horse fat	76–86
Animal oils		*Waxes*	
Tallow oil	55–57		
Neatsfoot oil	67–73	Spermaceti	2.6
Lard oil	69–75	Beeswax	8.5–11.5
Sperm	80–84	Wool fat	17–52
Bottlenose	80–85	Carnauba wax	55.2
Whale	116–128		
Shark	115–139		
Seal	130–152		
Codliver	138–167		
Menhaden	148–160		

Acetyl Value.—The estimation of the acetyl value as revised by Benedikt and Ulzer (*Monatsh.*, 1887, **8**, 41) is based upon the principle that hydroxy-acids, on being heated with acetic anhydride, exchange the hydrogen atom of their hydroxyl group or groups for the radicle of acetic acid. The operation is carried out by heating the free fatty acids with acetic anhydride.

Lewkowitsch (*Proc. Chem. Soc.*, 1890, **6**, 72, 91) drew attention to the causes of error in this process, and subsequently (*J. Soc. Chem. Ind.*, 1897, **16**, 503) devised the following method, which is now in general use: 10 grm. of the filtered fat are boiled for 2 hours with an equal volume of acetic anhydride in a round-bottomed flask beneath a reflux condenser, and the mixture then transferred to a large beaker, and boiled with several hundred c.c. of water, bumping being meanwhile prevented by passing a slow current of carbon dioxide through a long tube reaching nearly to the bottom of the beaker.

The mixture is allowed to separate into 2 layers, the water is siphoned off, and the oily layer again boiled out in the same manner until the last trace of acetic acid is removed. This is ascertained by testing with litmus paper. The acetylated product is freed from water and finally filtered through filter paper in a drying oven.

This operation may be carried out quantitatively, and in that case the washing is best done on a weighed filter. An increase of weight would prove that assimilation of acetyl groups had taken place. This method may be found useful to ascertain preliminarily whether a notable amount of hydroxylated acids is present in the sample under examination.

2 or 4 grm. of the acetylated substance are saponified by means of alcoholic potassium hydroxide solution as in the estimation of the saponification value. If the "filtration process" be used, the alcoholic alkali must be measured exactly, and this is also advisable with the distillation process, so as to obtain the saponification value of the acetylated fat. The alcohol is next evaporated and the soap dissolved in water.

From this stage the determination is carried out either by the (*a*) "distillation process" or (*b*) "filtration process."

(*a*) *Distillation Process.*—Add dilute sulphuric acid (1:10), in more than sufficient quantity to saturate the alkali, and distil as usual in Reichert's distillation process. Since several portions of 100 c.c. each must be distilled off, either a current of steam is blown through the suspended fatty acids or water is run into the distilling flask, from time to time, through a stoppered funnel fixed in the cork, or any other convenient device is adopted. It will be found quite sufficient to distil over 500 to 700 c.c., as the last 100 c.c. contain practically no acid. Filter the distillates to remove any insoluble acids carried over by the steam, and titrate the filtrates with N/10 potassium hydroxide solution, phenolphthalein being used as indicator. Multiply the number of c.c. by 5.61 and divide the product by the weight of substance taken. This gives the acetyl value.

(*b*) *Filtration Process.*—Add to the soap solution a quantity of standardised sulphuric acid exactly corresponding to the amount of alcoholic potassium hydroxide solution employed and warm gently, when the fatty acids will readily collect on the top as an oily layer. (If the saponification value has been estimated, it is, of course, necessary to take into account the volume of acid used for titrating back the excess of potassium hydroxide.) Filter off the liberated fatty acids, wash them with boiling water until the washings are no longer acid, and titrate the filtrate with N/10 potassium hydroxide solution, using phenolphthaleïn as indicator. The acetyl value is calculated in the manner shown above.

Both methods give identical results; the latter will be found shorter.

The acetyl value indicates the number of mg. of potassium hydroxide required for the neutralisation of the acetic acid obtained on saponifying 1 grm. of the acetylated fat or wax.

In the case of those oils and fats which have a high Reichert value, the apparent acetyl value will be too high, owing to the presence of the volatile acids. This influence will affect the distillation process to a greater extent than the filtration process. To eliminate this error, the volatile acids of the original oil or fat should be estimated in precisely the same manner, and the value thus obtained should be deducted from the apparent acetyl value.

It should be noted that in the case of a fat containing free alcohols (phytosterol, cholesterol), or, in the case of waxes, the acetyl value will be a measure of both the hydroxy-acids and the free alcohols. If present, acetic acid radicles are also absorbed by them. If the free alcohol is isolated its acetyl value may be determined as well. The difference between the acetyl value of the fat or wax and the acetyl value corresponding to the amount of free alcohol present will be the true measure of the hydroxy-acids.

If a free alcohol is acetylated, no complication through formation of anhydrides can arise, and in that case simply the saponification value of the acetylated product—the acetic ester of the alcohol—is determined. This value is also the acetyl value of the alcohol (the saponification value of the original alcohol being *nil*).

In a further study of the acetyl value, Lewkowitsch (*Analyst*, 1899, **24**, 319) has shown that it may indicate: 1. hydroxy-acids; 2. free alcohols; 3. oxidised fatty acids; 4. acids of unknown composition; 5. mono- and diglycerides, and 6. rancidity. Hence, until it is possible to determine to what extent these several factors contribute to the acetyl value, the latter cannot be regarded as a constant.

The following table gives some of the more important results obtained by Lewkowitsch (*loc. cit.*) by the above described processes:

Oil or fat	I	II	III
	Total volatile acids =mg. of KOH per grm.	Apparent acetyl value	True acetyl value II−I
Linseed	2.9	6.85; 6.92	3.98
Maize	2.53	8.21; 8.75	5.81
Curcas		7.5	
Castor	0.0	149.6–150.5	150.05
Colza	2.15	16.6; 17.2	14.75
Olive	2.54	12.78; 13.48	10.68
Horsesfoot	4.08	12.96; 14.40	9.44
Seal	1.50	16.47; 16.84	15.18
Codliver (old)	2.60	7.9; 8.9	5.8
Codliver (fresh)	3.60	4.75	1.15
Cottonseed	6.28	24.76; 25.1	15.65
Cottonseed	0.99	15.8	14.8
Palm (23% free acids)	2.34	17.8; 18.8	15.96
Cacao butter		2.71; 2.86	
Japan wax	10.05	27.3	17.25
Japan wax	5.6	31.2; 33.1	26.55
Lard	6.6; 6.7	9.3	2.65
Tallow	1.3	9.4; 10.4	8.6
Croton	21.07–21.09	40.68; 41.09	19.82
Palmnut	11.4	19.0	7.6
Coconut	20.9	23.2	2.3
Butter-fat	49.3; 49.4	48.48; 49.29	9.45
Butter-fat	43.32	45.23	1.91

OXIDATION OF OILS—DRYING PROPERTIES.

(See also under Linseed and other oils.)

Many of the fixed oils thicken on exposure to air, and, under favourable circumstances, gradually dry up into yellowish, transparent varnishes or resin-like substances, to which in the case of linseed oil the name *linoxyn* has been given. The nature of the oxidation changes that take place in the drying process is still very obscure, though the oils which possess this property in the most marked degree appear (except in the case of tung oil) to be characterised by a high proportion of linolenic and isolinolenic acids.

Strictly speaking, no hard and fast line can be drawn between different classes of oils as regards their drying properties, though for convenience of classification it is usual to group vegetable oils into *drying*, *semi-drying*, and *non-drying* oils.

An experimental investigation of the process of drying of linseed oil has been made by Genthe (*Zeit. angew. Chem.*, 1896, **19**, 2087), who shows that the presence of peroxides plays an important part in the process, and that polymerisation and formation of volatile acids accompany the oxidation. For other investigations of the theory of drying of oils see Livache (*Compt. rend.*, 1895, **120**, 842), and Fahrion (*Zeit. angew. Chem.*, 1891, 540; 1892, 171, and *Chem. Zeit.*, 1894, **17**, 1848).

For testing drying properties, a definite number of drops of the sample may be placed in a watch-glass or flat porcelain capsule, and exposed to a temperature of about 100° for 12 or 24 hours, side by side with samples of oil of known purity. Olive oil will be scarcely affected by such treatment, and rape oil will only become slightly thicker. Cottonseed oil will be considerably affected, while good linseed oil will form a hard skin or varnish, which can only with difficulty be ruptured by pressure with the finger. In some respects, a preferable plan is to flood a slip of glass with the oil to be tested, in the manner in which a glass-plate is covered with collodion. The glass with the adhering film of oil is then kept at 100°, and the progress of the drying followed by touching, at intervals, successive parts of the plate with the finger. Another useful method is to soak a definite measure of thick filter paper in the sample of oil, and then expose it to 100 or 130° for some hours, side by side, with samples of oil of known purity.

Livache's Method.—Livache has shown (*Compt. rend.*, 1886, **102**, 1167) that the absorption of oxygen is accelerated by the addition of finely-divided lead, and on this fact has based the following test, which enables numerical values to be obtained: About 1 grm. of lead[1] is accurately weighed and spread in a thin layer on a watch-glass, and 0.6 to 0.7 grm. of the oil allowed to drop from a pipette upon different parts of the lead, care being taken that they do not run into one another. The watch-glass is then weighed and allowed to stand exposed to the light at the ordinary temperature.

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[1] Prepared by precipitating a lead salt with zinc, washing the precipitate rapidly in succession with water, alcohol, and ether, and finally drying in a vacuum.

Drying oils will be found to have absorbed the maximum quantity of oxygen after 18 hours, or in some cases after 3 days, whereas non-drying oils do not gain weight until the fourth or fifth day.

The free fatty acids, with the notable exception of cottonseed-oil acids, behave like the oils, *i. e.*, their increase in weight corresponds to the gain in weight of the corresponding neutral oils. Livache's results were as follows:

	Gain in weight of 100 parts		
	Of oil after		Of fatty acids after
	Two days	Seven days	Eight days
Linseed oil	14.3	..	11.0
Walnut oil	7.9	..	6.0
Poppyseed oil	6.8	..	3.7
Cottonseed oil	5.9	..	0.8
Beechnut oil	4.3	..	2.6
Colza oil	0.0	2.9	2.6
Rape oil	0.0	2.9	0.9
Sesame oil	0.0	2.4	2.0
Arachis oil	0.0	0.8	1.3
Olive oil	0.0	1.7	0.7

To obtain a correct estimate as to the drying properties of an oil, regard must be had not only to the increment in weight, but also to the length of time required. Thus, of the two oils in the following table, No. 1 must be considered the better, although both finally reach the same absorption of oxygen:

No. of oil	Weight of oil	Weight of lead	Gain in weight of 100 parts after			
			One day	Three days	Six days	Nine days
1	3.246	1.012	14.4	15.7	unchanged	..
2	3.154	0.653	2.45	12.0	15.9	unchanged

Bishop's method (*J. Pharm. Chim.*, 1896, [6], **5**, 55) in which the oil is mixed with precipitated silica and manganese resinate (as an oxygen carrier) gives the results more rapidly, but has not yet displaced Livache's method as a practical test.

Oxygen Absorption:—The tendency of fixed oils to absorb oxygen is in direct proportion to their capacity of absorbing bromine or iodine, and to the rise of temperature produced on treating them with sulphuric acid. This is shown by the fact that it is possible to obtain "ozone values" of oils corresponding to the iodine values as was shown by Fenaroli (*Gazzetta*, 1906, **36**, 292). When dry ozone is allowed to bubble through an oil at a temperature not exceeding 40°, the increase in weight of the oil exactly corresponds to an addition of 1 mol. of ozone for each double-bond in the mol. of the fat.

Spontaneous Combustion.—Gellatly has pointed out the close relationship which exists between the drying properties of oils and their tendency to inflame spontaneously when exposed to the air in a finely divided condition. Useful forms of apparatus for testing the liability of oils to spontaneous combustion have been devised by Allbright and Clark (*J. Soc. Chem. Ind.*, 1892, **11**, 547) and by Mackey (*ibid.*, 1895, **14**, 940). In the latter, 7 grm. of cotton-waste previously soaked in 14 grm. of the oil, are placed in a roll of wire gauze 5 inches square (24 meshes to the inch), and the whole placed in a water-oven in which the water is boiling. A thermometer is passed through the opening of the oven, so that its bulb reaches to the centre of the wool in the wire roll, and the temperature is taken at regular intervals. All oils that take fire or attain a temperature of over 200° in less than 2 hours in this test must be regarded as dangerous. (See p. 512.)

Oxidised Oil. Blown Oil. Base Oil.—The commercial products sold under these names are produced by blowing a stream of air through a fatty oil—rape, cottonseed, or linseed oil being usually chosen for the purpose. A certain initial temperature is necessary to start the action, but afterwards the heat produced by the oxidation is sufficient to maintain the temperature required. By proper regulation, products can be obtained which closely simulate castor oil, and equal that body both in sp. gr. and viscosity. Methods of distinguishing blown oils from castor oil are given in the section treating of the latter product.

ELAIDIN REACTION.

When oleic acid is exposed to the action of nitrogen trioxide, it is gradually converted into the isomeric body elaidic acid, which is solid at ordinary temperatures. Olein undergoes a similar change, being converted into the solid elaidin, as do also oils in which olein predominates. On the other hand, drying oils, in which the chief constituents are linolenic and linolic acids, are not visibly affected by treatment with nitrous acid; and oils largely consisting (probably) of a mixture of olein and linolin give less solid products than those with olein as a main constituent.

The effect can be produced by the gas evolved on heating starch or arsenous oxide with nitric acid; by a mixture of a nitrite with a dilute acid; by dissolving copper or mercury in nitric acid under a layer of the oil; by agitating the oil with a freshly prepared solution of mercurous nitrate; by the direct use of nitric acid of yellow or reddish color, and therefore containing lower oxides of nitrogen; and, lastly, by heating the oil with nitric acid until chemical action sets in and gaseous oxides of nitrogen are evolved.

Poutet's Elaidin Test.—The following method of applying the test devised in 1819 by Poutet is in use in the Paris Municipal Laboratory: 1 grm. of mercury, 5 grm. of nitric acid (sp. gr. 1.35 to 1.41) and 10 grm. of the oil to be tested, are shaken together for 3 minutes in a test-tube, which is then left for 20 minutes, and finally shaken again for 1 minute. The changes that subsequently take place are then noted, including the time required for solidification when that occurs.

Archbutt's Modification (*J. Soc. Chem. Ind.*, 1886, **5**, 304) gives more constant results than the above-described method. The reagent is prepared by dissolving 18 grm. of mercury in 15.6 c.c. of nitric acid of sp. gr. 1.42 (22.2 grm.) in a stoppered cylinder, 1 part (8 grm.) of the resulting green solution is shaken with 12 parts (96 grm.) of the oil under examination in a wide-mouthed bottle, which is then closed with a stopper and placed in water maintained at a constant temperature (not lower than 25°), and shaken at intervals of 10 minutes for 2 hours. The time required for solidification is of greater importance than the consistency of the product.

The behaviour of the more important liquid fixed oils, when tested in the foregoing manner, is as follows:

A hard mass is yielded by olive oil, almond oil, arachis oil, lard oil, sperm oil, and sometimes neatsfoot oil.

A product of the consistence of butter is given by neatsfoot, bottlenose mustard, and sometimes by arachis, sperm, and rape oils.

A pasty or buttery mass which separates from a fluid portion is yielded by rape (mustard), sesame, cottonseed, sunflower, nigerseed, cod-liver, seal, whale, and porpoise oils.

Liquid products are yielded by linseed, hempseed, walnut, and other drying oils.

In practice, the elaidin test receives its most important application in the examination of olive oil, with which it gives a very characteristic result. The subject is further discussed in the sections treating of olive and rape oils.

Investigations of the elaidin reaction and attempts to apply it quantitatively have been made by Farnsteiner (*Zeit. Unters. Nahr. Genussm.*, 1899, **2,** 1); by Edmed (*Proc. Chem. Soc.*, 1899, **15,** 190); and by Lidow (*Pharm. Zeit. Russland.*, 1895, **34,** 105; *Analyst*, 1895, **20,** 178).

Interaction of Oils with Sulphur Chloride.—The vegetable drying oils are converted, on treatment with sulphur chloride (S_2Cl_2), into gelatinous or elastic masses, which are employed as substitutes for india-rubber. Bruce Warren investigated the reaction with a view to its employment in the analysis of oils (*Chem. News*, 1888, **57,** 113).

COLOUR TESTS OF OILS.

Many fatty oils give coloured products when treated with chemical reagents, and in some cases these afford valuable means of detecting even small quantities of special oils in admixture with other oils.

The most characteristic of these tests for special oils are Becchi's and Halphen's tests for cottonseed oil and the Baudouin test for sesame oil; these are described under the special sections dealing with those oils.

Little value can be placed on the results of most of the older colour-sts described by Calvert and Chateau, since the particular colorations were often due to accidental impurities in the oils. The tests with sulphuric and nitric acid, however, have some value, especially when applied simultaneously to specimens of oil of known purity.

Sulphuric Acid Colour Test.—The addition of 1 or 2 drops of strong sulphuric acid to 20 drops of the oil produces colorations which, when observed both before and after stirring, are sometimes characteristic. Thus, vegetable non-drying oils often give a light greenish-brown colouration, whilst the colours obtained with the more unsaturated drying oils are red-brown to dark brown. Hydrocarbon oils also become dark brown and show a characteristic blue fluorescence. The greater degree of coloration produced by more unsaturated oils is probably to be attributed largely to the effect of the heat produced in the chemical interaction of the oil and acid.

The sulphuric acid test has a greater value in the examination of cod-liver and other marine animal oils, since the presence of cholesterol and lipochromes in these oils causes the production of characteristic colorations. The colours may be rendered indistinct, however, by the charring action exerted by the reagent. This may be avoided by dissolving 1 drop of the oil in 20 drops of carbon disulphide, and agitating the solution with a drop of strong sulphuric acid. Whale oil, when thus treated, gives a fine violet coloration, quickly changing to brown, whereas with sulphuric acid alone a red or reddish-brown colour changing to brown or black is obtained.

Nitric Acid Colour Test.—This is useful as a test for the presence of cottonseed oil in olive and other non-drying oils. 5 c.c. of the oil under examination are shaken with an equal quantity of nitric acid of sp. gr. 1.37, and the mixture left for 24 hours. In the presence of even a small percentage of cottonseed oil there should be a more or less pronounced brown coloration.

PHYSICAL PROPERTIES.

The general characteristics of the fixed oils have already been described. Some of their physical properties are of importance for their recognition and estimation, this being especially true of their sp. gr., melting and solidifying points, absorption-spectras refractive indices, viscosity, and behaviour with solvents. The methods of ascertaining these characteristics are described in detail in the following sections.

Cohesion-figures of Oils.—The surface-tension of oils may in certain cases be capable of useful application, though its value has been much exaggerated. When a drop of oil is allowed to fall gently on to the surface of water, it often behaves in a characteristic fashion, first spreading out and then contracting, forming figures which differ with the nature of the oil. Descriptions and illustrations of typical cohesion-figures are given in Alder Wright and Mitchell's *Oils, Fats and Waxes*, 1905, p. 50.

Absorption-spectra of Oils.—The absorption-spectra of the fixed oils occasionally afford valuable indications of their purity. For observing them a micro-spectroscope may be used, but in many cases the light must be caused to pass through several cm. of the oil to be examined. Although some vegetable oils give exceedingly striking absorption-bands, these are due not to the oils themselves but to the chlorophyll and impurities contained in them. Hence the purification or clarification of an oil tends to reduce the characteristic nature of the absorption-bands, which, indeed, may disappear altogether if the oil be long exposed to sunlight. In one particular, however, the absorption-spectrum furnishes important information. Thus, no oils of animal origin give definite absorption-bands, the spectrum being merely obscured at the more refrangible end, whilst in many vegetable oils the absorption-bands of chlorophyll are exceedingly well marked, especially a band having about the same refrangibility as the line termed B. In this way it is easy to detect the presence of rape, olive, or linseed oil in sperm, cod, or lard oil. Castor and almond oil, on the other hand, give no well-defined bands, and the band at B in the case of sesame oil is faint, though there is strongly marked absorption of the whole of the red portion nearly up to that point.

Patterson (*J. Soc. Chem. Ind.*, 1890, **9**, 36) devised a special absorption spectrum colorimeter for the spectroscopic examination of oils. (See also Introduction to Vol. 1.)

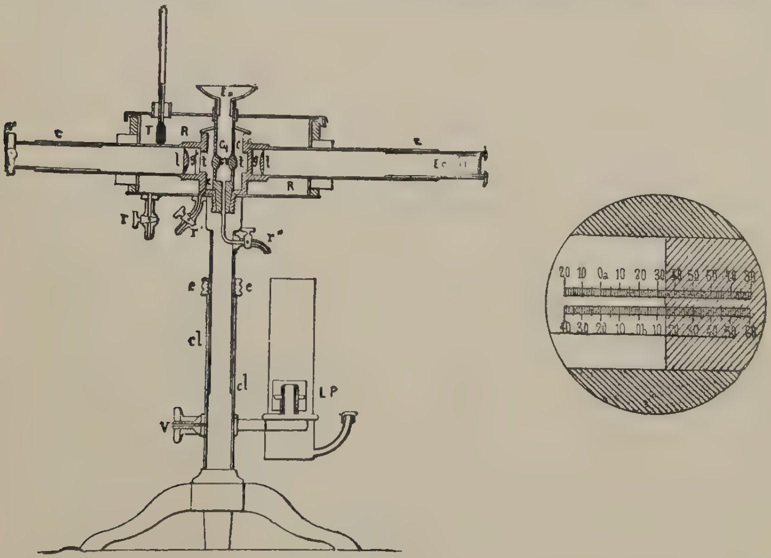
Refractive Power.—Valuable indications as to the purity of fats and oils, especially butter-fat, may be gained from the observation of the refractive index. The instrument in general use for this purpose is the *butyrorefractometer*, which is described in the section dealing with BUTTER. In certain cases, however, such as tung oil and rosin oils, the indices are outside the scale of the butyrorefractometer, and recourse must be had to the earlier instrument of Abbé.

Abbé's Refractometer.—The following method of using this instrument is prescribed by the A. O. A. C.:

A piece of fine tissue paper, 3 cm. in length by 1.5 cm. in width, is placed on the lower of the two glass prisms of the apparatus. Two or three drops of the sample are placed upon the paper, and the upper prisms carefully fixed in position, so as not to move the paper from its place. In charging the apparatus with the oil in this way it is placed in a horizontal position. After the paper disc holding the fat is secured by replacing the upper prism, the apparatus is placed in its normal position, and the index moved until the light directed through the apparatus by the mirror shows the field of vision divided into dark and light portions. The dispersion apparatus is now turned until the rainbow colours on the part between the dark and light fields have disappeared. Before doing this, however, the telescope, the eye-piece of the apparatus, is so adjusted as to bring the cross-lines of the field of vision distinctly into focus. The index of the apparatus is now moved back and forth until the dark edges of the field of vision fall exactly in the intersection of the cross-lines. The refractive index of the fat under examination is then read directly upon the scale by means of a small magnifying glass. To check the accuracy of the first reading, the dispersion apparatus should be turned through an angle of 180° until the colours have again disappeared, and the scale of the instrument again read. These 2 readings should nearly coincide, and their mean is the true reading.

For butter-fats the apparatus should be kept in a warm place, the temperature of which does not fall below 30°. For reducing the results to a standard temperature, say 25°, deduct 0.000176 for every degree above that point, since, as the temperature rises, the refractive index falls. The instrument used should be set with distilled water at 25°, the theoretical refractive index of water at that temperature being 1.3330.

Oleorefractometer.—The instrument devised by Amagat and Jean (*Compt. rend.*, 1889, **109**, 616) enables a very rapid comparison to be made between the refractive power of a given oil and that of a genuine oil taken as a standard. The oil to be observed is introduced into a hollow prism, which is immersed in a vessel with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40 30 20 10 0b 10 20 30 40 50 60

FIG. 3.—Jean's Oleorefractometer. (*Baird and Tatlock.*)

parallel sides filled with a standard oil. If the refractive power of the sample is the same as that of the standard, no deviation of the ray of light traversing the apparatus will take place; but otherwise deviation will occur, and can be measured on a micrometer-scale placed on the eye-piece. The angle of the prism, the neutral or standard oil, and the division of the scale are all arbitrary. The standard oil sold with the instrument is sheepsfoot oil.

In the figure, *t t* represent circular metal vessel with 2 opposite lenses, *l l* in front of the glass sides. From these extend the 2 tubes C and L, the former terminating in a collimator, V, and the latter in a telescope, O*c*. The glass prism-cell is represented by C*y*, whilst E*c* is an arbitrary photographic scale. The instrument is illuminated by means of a gas-jet, and the luminous field may be divided by means of a slide into a light and dark portion.

In using the oleorefractometer, the outer vessel is charged with the standard oil (which gives a zero reading), the oil to be tested placed in the inner vessel, and an outer trough (not shown) filled with water. The temperature is then brought to 22° by means of the lamp, L P, and the deviation read upon the scale.

The following results were obtained by Pearmain (*Analyst*, 1895, **20,** 135) with this instrument:

Oil or fat	No. of samples	Deviation	Highest	Lowest	Average
Temperature 22°.					
Almond	8	+	10.5	8.0	9.5
Arachis	5	+	7.0	5.0	6.0
Bottlenose	1	+	50.0	50.0	50.0
Cabbage seed	1	+	15.0	15.0	15.0
Castor	8	+	42.0	39.0	40.0
Codliver	8	+	46.0	40.0	44.0
Cottonseed (crude)	3	+	17.0	16.0	16.5
Cottonseed (refined)	6	+	23.0	17.0	21.5
Hempseed	4	+	37.5	34.0	35.5
Lard oil	6	−	1.0	0.0	0.0
Linseed (crude)	3	+	52.0	48.0	50.0
Linseed (refined)	5	+	54.0	50.0	50.0
Neatsfoot	2	−	3.0	1.0	2.0
Nigerseed	2	+	30.0	26.0	28.0
Olive	105	+	3.5	1.0	2.0
Peach kernel	2	+	11.5	7.5	9.5
Pilchard	2	+	36.0	32.0	34.0
Poppy seed	3	+	35.0	30.0	33.0
Rape	8	+	20.0	16.0	17.5
Ravison	2	+	24.0	20.0	22.0

Oil or fat	No. of samples	Deviation	Highest	Lowest	Average
Temperature 22°.					
Seal	2	+	36.0	30.0	33.0
Sesame	5	+	17.0	13.0	15.5
Shark	3	+	35.0	29.0	31.0
Sunflower	1	+	35.0	35.0	35.0
Tallow oil	2	−	5.0	1.0	3.0
Tea seed	1	+	8.0	8.0	8.0
Tung	1	+	75.0	75.0	75.0
Whale	2	+	48.0	42.0	45.0
Oleic acid	3	−	33.0	29.0	32.0
Temperature 45°.					
Butter-fat	15	−	34.0	25.0	30.0
Margarine	7	−	18.0	13.0	15.0
Lard	10	−	14.0	8.0	10.5
Tallow	6	−	18.0	15.0	16.0
Paraffin (soft)	2	+	58.5	54.0	56.0

Action on Polarised Light.—Most of the vegetable oils in common use are either neutral or slightly lævorotatory (−0.1° to −1.5° in a 200 mm. tube in the polarimeter). Hence, rosin oil, which is strongly dextrorotatory, may often be detected by means of this test in drying oils. Olive oil and sesame oil have a slight dextrorotation, whilst castor oil and croton oil (*q. v.*) are strongly dextrorotatory. For the values obtained with various oils see Alder Wright and Mitchell's *Oils, Fats and Waxes*, 1903, p. 52, and Peter, *Bull. Soc. Chem.*, 1887, [2], **48**, 483.

Electrical Conductivity.—The measurement of the specific resistance offered by solutions of the potassium soaps obtained under standard conditions from different oils and fats affords a means of distinguishing between them. A method was devised by Herlant (*Bull. de l'Ass. belge Chim.*, 1896, **10**, 48).

Heat of Combustion.—Measurement of the heat of combustion of different oils and fats may be used in their analytical differentiation and in obtaining data as to their food value. A table of the values obtained with the different fatty acids is given by Stohmann, Kleber, Langbein and Offenhaur (*J. pr. Chem.*, 1894, **49**, 99); while results obtained with various oils and fats and their adulterants are given by Schweinitz and Emery (*J. Amer. Chem. Soc.*, 1896, **18**, 174) and Sherman and Snell (*ibid.*, 1901, **23**, 164). For the detection of adulteration the heat of combustion offers no advantage over simpler methods of analysis.

Viscosity.—A useful physical test for oils is based on their relative "body" or viscosity, a property which may be regarded as the converse of fluidity. The viscosity is usually compared with that of rape oil, but it may also be referred to water or glycerol as a standard. The subject is fully discussed in the section on the "Examination of Lubricating Oils."

Specific Gravity.—The sp. gr. of the fixed oils and fats is a property largely dependent on their constitution, and hence is more or less characteristic of each particular oil. As a rule, the sp. gr. of different samples of the same kind of oil varies within very narrow limits, but it is liable to be affected by the treatment to which the oil may have been subjected in the process of refining, the presence of free fatty acids, the age of the oil, and the amount of oxidation it has undergone, and by other circumstances.

The sp. gr. of fixed oils may be ascertained by the usual methods, but great care is necessary. Owing to the high coefficient of expansion of oils, the temperature at which the observation is made should be carefully noted, and in accurate observations the thermometer employed should be an instrument the indications of which have been verified.

When a sufficient quantity of the sample is available, and results of extreme accuracy are not required, sp. gr. can be ascertained readily and satisfactorily by means of an accurate and delicate hydrometer. In any observations, save those of the roughest kind, the oil should be brought accurately to the standard temperature by immersing the hydrometer-glass in water, cooled, if necessary, to 15.5° by dissolving in it sodium thiosulphate or ammonium nitrate. The hydrometer should be immersed in the oil for 5 or 10 minutes, and the temperature again observed before taking a reading of the sp. gr., as the use of a warm hydrometer may cause an increase of several degrees in the temperature of the oil. Of course, in taking sp. gr. by a hydrometer, the accuracy of the instrument employed is presupposed, but many of the instruments sold are inaccurate to the extent of several degrees.

The sp. gr. bottle and Sprengel-tube (see Vol. 1) may also be employed for ascertaining sp. gr. of oils, and allow of more accurate estimations than can be made with a hydrometer. The weight of distilled water which the bottle or tube holds at a temperature of

15.5° is usually (at least in England) taken as the unit of comparison in stating the sp. gr. of fixed oils.[1]

Solid Fats and Waxes.—As many of the fixed oils are solid or semi-solid at the ordinary temperature, their sp. gr. are not directly comparable with those of the fluid oils. This difficulty may be obviated by taking the sp. gr. of the melted substance at some higher temperature, preferably the b. p. of water. This may be done with a hydrometer or balance, if the cylinder containing the oil be kept for a sufficient time in boiling water before the reading is taken. A sp. gr. bottle is less convenient, but with the Sprengel-tube great accuracy is possible. The weight of the Sprengel-tube and of the volume of water it contains at 15.5° being known, the tube should be completely filled with the oil, by immersing one of the orifices in the liquid and applying suction at the other. The tube is placed in a conical flask containing water which is kept vigorously boiling, a porcelain crucible-cover being placed over the mouth of the flask. The oil expands and drops from the orifices. When this ceases, the oil adhering to the outside is removed by the cautious use of filter-paper, the tube removed, wiped dry, cooled, and weighed. The weight of the contents divided by the weight of water contained at 15.5° will give the sp. gr. at 100° compared with water at 15.5°.

When the amount of material is sufficient, the observation may be made by means of the plummet (Westphal's balance), the use of which leaves nothing to be desired on the score of rapidity, accuracy, or ease of manipulation. In taking sp. gr. by the plummet at the b. p. of water, it is desirable to employ a cylindrical bath of metal (Fig. 4), the top of which is perforated by two orifices. One of these is fitted with an upright tube, which serves to convey the steam away from the neighbourhood of the balance, while into the other a test-tube, 6 in. in length and 1 in. in diameter, fits tightly, the joint being made perfect by a ring of cork or india-rubber. The test-tube is filled with the oil, the sp. gr. of which is to be ascertained, and the plummet immersed in it. The water in the outer vessel is then kept in constant ebullition, until a thermometer, with which the oil is repeatedly stirred, indicates a constant temperature, when the plummet is attached to the lever of the balance, and counterpoised in the usual way. (See also Vol. 1 for improved methods of ascertaining sp. gr.)

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[1] Oil merchants frequently use a hydrometer on which water is marked 0° and rape oil 28°.

Hager has devised an ingenious method of ascertaining the sp. gr. of solid fats at the ordinary temperature. The fat is melted and drawn up into a pipette, from which it is allowed to drop slowly from the height of 2.5 cm. into cold alcohol contained in a flat-bottomed dish, care being taken that each drop of fat falls in a different place. An alternative plan is to melt the fat in a small-lipped capsule and allow drops of it to fall on a plate of glass which has been previously wiped with a wet cloth. On placing the glass in cold water, the drops usually become detached on the slightest touch, but if necessary can be removed with a knife after half an hour. The fat-globules obtained by one of the above methods are removed to a beaker containing dilute alcohol. The sp. gr. of the liquid is then adjusted by addition of alcohol or water, till, after careful stirring, the fat-globules remain in equilibrium in any part of the liquid at a temperature of 15.5°. Ammonia may be substituted for the spirit if preferred. The sp. gr. of the liquid is then taken, and the result obtained recorded as the sp. gr. of the suspended fat. The great objection to this method is that fats and waxes which have undergone sudden cooling have abnormal sp. gr. On this account it is far preferable to employ for the experiment fragments which have been cut off a mass cooled under normal conditions.

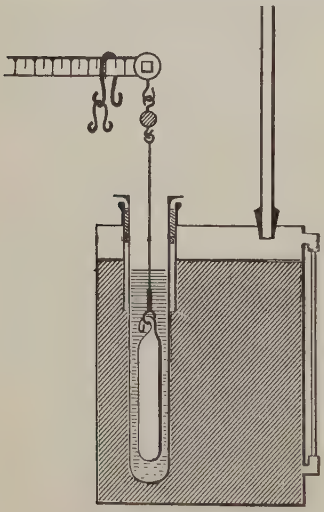

FIG. 4.

A good method of preparing beeswax and other waxes for this test is to pour the melted substance into a cylinder about 0.5 inch in length cut from narrow glass tubing. The lower end of this is kept pressed against a glass plate until the wax solidifies, after which the outside of the glass is gently warmed, and the core of wax pushed out, and allowed to stand for some hours at the ordinary temperature. It is then brushed over with dilute alcohol, to prevent the subsequent occurrence of air-bubbles, and is immersed in spirit which is diluted or strengthened until of the same sp. gr. as the wax.

The following table shows the sp. gr. (observed by Allen) at different temperatures of various fats and other substances which are solid at the ordinary temperature. In each case the examinations were made on the same sample of substance by the plummet method. A column is added showing the difference in sp. gr. corresponding to a change of 1°.

The values obtained at the higher temperature were not corrected for the expansion of the glass plummet of the apparatus, and hence many of them are too low by about 0.01 to 0.02.

Nature of fat, etc.	Sp. gr. of melted fats, etc.; water at 15.5° C. (60° F.) = 1,000		Difference for 1°
Palm oil	893.0 at 50°	858.6 at 98°	0.717
Cacao butter	892.1 at 50°	857.7 at 98°	0.717
Japan wax	901.8 at 60°	875.5 at 98°	0.692
Tallow	895.0 at 50°	862.6 at 98°	0.673
Lard	898.5 at 40°	860.8 at 98°	0.650
Butterine	898.2 at 40°	859.2 at 98°	0.672
Butter-fat	904.1 at 40°	867.7 at 99°	0.617
Coconut stearin	895.9 at 60°	869.6 at 99°	0.674
Coconut oil	911.5 at 40°[1]	873.6 at 99°[1]	0.642
Palmnut oil	911.9 at 40°[1]	873.1 at 99°[1]	0.657
Spermaceti	835.8 at 60°	808.6 at 98°	0.716
Beeswax	835.6 at 80°	822.1 at 98°	0.750
Carnaüba wax	850.0 at 90°	842.2 at 98°	0.975[2]
Stearic acid (commercial)	859.0 at 60°	830.5 at 98°	0.750
Oleic acid (commercial)	903.2 at 15.5°	848.4 at 99°	0.656
Paraffin wax	780.5 at 60°	753.0 at 98°	0.724

The figures in the foregoing table represent merely the sp. gr. possessed by *particular samples* of different oils. The limits of variation of sp. gr., and the value of it as a means of recognising and estimating the amount of the various fixed oils in mixtures are discussed in a separate section.

Coefficients of Expansion.—It is always desirable to determine the sp. gr. of oils at the standard temperature, but in many cases in which this cannot be done a suitable correction may be made. The *rate of expansion* of an oil may be found by estimating the sp. gr. at two given temperatures as far apart as possible.[1] The rates of expansion of the solid fats, etc., are given in the table on page 51, while from the figures recorded on page 49 Allen calculated the rates of expansion of various oils fluid at ordinary temperatures. The following table shows the values so obtained, together with certain data published by other observers:

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[1] The samples of coconut oil and palmnut oil were old, and had been frequently melted. Some time previously they showed sp. gr. notably less than the figures stated in the table.

[2] For obvious reasons, the rate of expansion of carnaüba wax is only a rough estimation.

Nature of oil	Correction for 1°	Observer	Nature of oil	Correction for 1°	Observer
Sperm oil.......	0.648	A. H. Allen	Olive oil.......	0.629	C. M. Stillwell
Bottlenose oil...	0.643	A. H. Allen	Arachis oil.....	0.655	A. H. Allen
			Rape oil.......	0.620	A. H. Allen
Whale oil.......	0.697	A. H. Allen	Sesame oil.....	0.624	A. H. Allen
Whale oil.......	0.722	C. M. Wetherill	Cottonseed oil..	0.629	A. H. Allen
Porpoise oil.....	0.654	A. H. Allen	Coconut olein..	0.665	A. H. Allen
Seal oil.........	0.615	A. H. Allen			
Shark-liver oil ..	0.648	A. H. Allen	Nigerseed oil...	0.637	A. H. Allen
Codliver oil	0.646	A. H. Allen	Linseed oil.....	0.649	A. H. Allen
Menhaden oil...	0.654	A. H. Allen			
			Castor oil......	0.653	A. H. Allen
Neatsfoot oil ...	0.625	A. H. Allen			
Lard oil........	0.658	C. M. Wetherill			

It is evident that the *coefficient of expansion* of an oil may be deduced by dividing the temperature-correction by the sp. gr. Thus the coefficient of expansion of olive oil will be $\frac{0.646}{916}=0.000715$ for each degree centigrade.

From the foregoing data Wright (*J. Soc. Chem. Ind.*, 1907, **26**, 513) has calculated the numerical value of the approximate *modulus of expansion, m.* If S_o,S_t, and S_T represent the sp. gr. of the same fat at the respective temperatures O°, $t°$ and T° (water at $15.5°=1$) then

$$S_t=S_0(1-mt),$$

$$\text{and } S_T=S_0(1-mT),$$

The mean value of the m in the case of the 30 oils, etc., examined by Allen is approximately 0.0007; whence is obtained the equation

$$\frac{St}{ST}=\frac{1-0.007t}{1-0.0007T};$$

or if $t=15.5°$.,

$$S_{15.5}=ST\times\frac{0.98915}{1-0.0007T}$$

---

[1] Thus a sample of rape oil was found to have a sp. gr. of 915.0 at 15.5°, and 863.2 at 98°, the difference being 51.8. Dividing this by 82.5, the difference between the temperatures at which the observations were made ($98.0-15.5=82.5$), the figure 0.628 is obtained as the correction to be made for a variation of 1° from the standard temperature.

The following table gives the value of this factor for each degree from 10° to 25°., so that the sp. gr. of any oil, fat or wax estimated at a temperature other than 15.5° may be rapidly corrected to the latter temperature.

At °	Factor	At °	Factor
10	$\frac{1}{1.00389}$	18	1.00177
11	$\frac{1}{1.00318}$	19	1.00248
12	$\frac{1}{1.00248}$	20	1.00319
13	$\frac{1}{1.00177}$	21	1.00391
14	$\frac{1}{1.00106}$	22	1.00462
15	$\frac{1}{1.00035}$	23	1.00534
16	1.00035	24	1.00605
17	1.00106	25	1.00677

Melting and Solidifying Points.—The observation of the solidifying point of an oil is often of considerable importance, especially in the case of lubricating oils, in which too high a m. p. is a decided disadvantage. Similarly, the suitability of the solid fats for many of the purposes to which they are applied is greatly dependent on their m. p.

Entire uniformity of solidifying or melting-point in the case of particular oils and fats is not to be expected, as the natural fats consist of a mixture of liquid and solid substances, the proportions of which may vary considerably in different samples of what is nominally the same substance. Moreover, the melting-points, like the sp. gr. of the natural oils and fats, are liable to obscure alterations on keeping, and are further modified by the presence of varying amounts of free acid.

It has also been observed that many of the fats solid at the ordinary temperature have at least two distinct m. p. Thus the ordinary clarified tallow of commerce, if previously melted at a temperature considerably above its m. p., shows a m. p. of 35° to 36°. If it be carefully remelted at that temperature, cooled, and the m. p. again taken, the reading will sometimes be found nearly 12° above the former estimation.

This phenomenon of *double m. p.*, which is a striking characteristic of the mixed glycerides isolated from various fats, has been shown by Grün and Schacht (*Ber.*, 1907, **40**, 1778) to be due to the existence of two isomeric modifications of such glycerides, the one of lower m. p. being the more unstable, and undergoing gradual transformation into the modification of higher m. p.

Melting Point.—The substance is melted at a temperature slightly above its fusing point, and drawn up into a very narrow glass tube (made by drawing out one end of a piece of ordinary quill tubing), where it is allowed to solidify spontaneously. After an interval of *not less than 1 hour and preferably 12 hours* the tube, open at both ends, is attached by a cork or india-rubber ring to the stem of a thermometer in such a manner that the part of the tube containing the substance is at the same level as, and in close proximity to, the bulb. The thermometer, with its tube, is then immersed in water, which is gradually heated at a rate not exceeding 0.5° per minute until fusion of the contents of the capillary tube takes place, when the temperature is recorded. The flame is then removed, and the temperature at which the fat resolidifies also observed. In cases in which the melting and solidifying points are not notably different, it is usual to record the mean of the two as the true m. p. of the substance. It is desirable to immerse the beaker of water containing the thermometer in an outer vessel also filled with water, and to apply the source of heat to the latter. A 500 c.c. flask, from which the neck has been cut off, filled to the brim (Fig. 5), furnishes a very convenient water-bath, and allows of a very regular and gradual heating of the water contained in the beaker placed in its mouth.

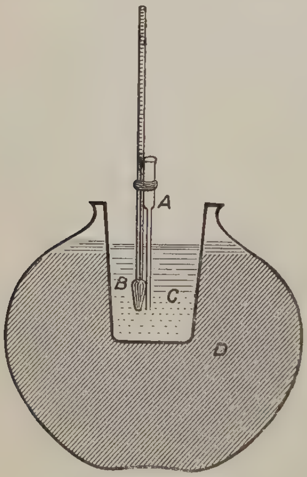

FIG. 5.

The foregoing method is applicable only to bodies melting above the freezing point of water, but by substituting strong brine for the water, much lower temperatures may be observed.

By using a tube with its capillary end sealed up, and placing the fat in the upper part of the tube, the *softening point*, which is frequently appreciably lower than the m. p. (the temperature at which the fat falls to the bottom of the tube), may be ascertained, while the point of resolidification is also more accurately observed than is possible in an open tube.

The method of ascertaining the softening point devised by Bevan and Cross (*J. Chem. Soc.*, 1882, **41**, 111) gives very accurate results, and is specially suitable for cases in which the fat does not melt readily (see Fig. 6).

A very thin piece of sheet-iron (ferrotype plate) is cut into an elliptical form, about 1 in. long by 1/2 in. wide. At one of the foci (A) a small depression is made, and at the other a hole (B) is cut, of such size as to allow the plate to be fixed on to the elongated bulb of a thermometer (C), so as to project therefrom at right angles. A glass float (D) is made by blowing a small bulb at the end of a capillary glass tube about 3 in. long, a small looped or hoe-shaped piece of platinum wire (E) being sealed into the bulb at the end opposite the stem of the float. To make an observation, a very small quantity of the sample is melted in the indentation of the iron-plate; and, while still liquid, the loop or hoe of the platinum wire of the float is immersed in it and allowed to become fixed by the spontaneous solidification of the substance, the stem of the float being supported in a vertical position. A thermometer is then cautiously introduced into the hole in the plate, and with it supported in a small beaker, which is then filled with mercury or other liquid. This is then gradually heated till the substance under observation melts, when the float is released and instantly rises to the surface of the liquid. The results are very concordant, and free from certain sources of error to which observations made by the capillary-tube method are liable.

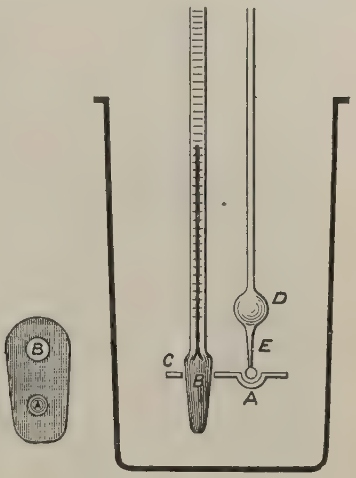

FIG. 6.

A very rapid method of ascertaining both the temperature of incipient fusion and that of complete liquefaction is to place fragments of the material upon the surface of clean mercury (previously chilled if necessary) in a small basin, which is placed on a water-bath. The temperature is very gradually raised, and the point at which the substance changes its form is ascertained by means of a sensitive thermometer.

Modifications of this method, in which the substance, on fusing, completes an electric circuit and rings a bell, have been devised by Loewe (*Dingler's polyt. J.*, 1871, **201,** 250) and Christomanos (*Ber.*, 1890, **23,** 1098), and an arrangement of the kind is in use in the Paris Municipal Laboratory.

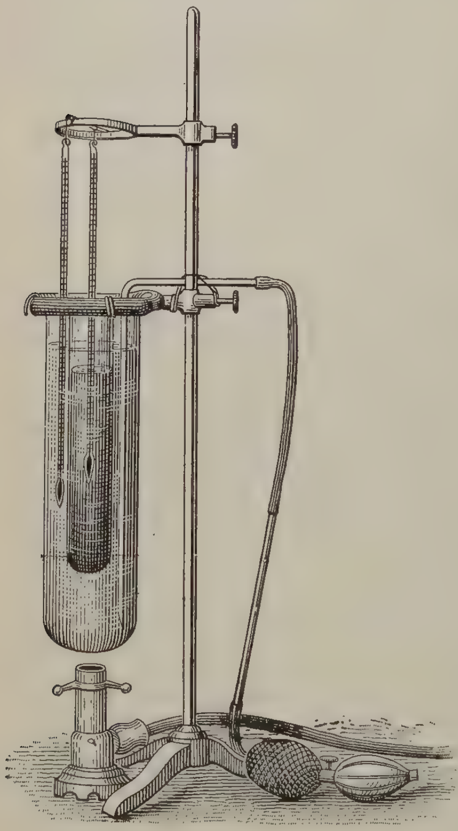

Fig. 7.

A. O. A. C. Method.—The melted and filtered fat is allowed to fall from a dropping-tube from a height of from 15 to 20 cm. on a smooth piece of ice floating in distilled water that has been recently boiled. The discs thus formed are from 1 to 1.5 cm. in diameter, and weigh about 200 mg. By pressing the ice under the water the discs are made to float on the surface, whence they are easily removed with a steel spatula, which should be cooled in the ice-water before using.

The apparatus (see Fig. 7) consists of a test-tube 30 cm. long and 3.5 cm. in diameter, supported in a boiling tube 35 cm. long and 10 cm. in diameter. The test-tube contains a mixture of alcohol and water prepared by separately boiling distilled water and 95% alcohol for 10 minutes to remove the gases which they may hold in solution. While still hot, the water is poured into the test-tube until it is nearly half full. The test-tube is nearly filled with the hot alcohol, which is carefully poured down the side of the inclined tube to avoid too much mixing. If the alcohol is not added until the water has cooled, the mixture will contain so many air-bubbles as to be unfit for use. These bubbles will gather on the disc of fat as the temperature rises and finally force it to the top. The test-tube containing the alcohol and water is placed in the boiling tube containing water and ice, until cold. The disc of fat is then dropped into the tube from the spatula and at once sinks to the part of the tube in which the sp. gr. of the diluted alcohol is exactly equivalent to its own.

A sensitive thermometer graduated in tenths of a degree is now lowered into the test-tube until the bulb is just above the disc, and is subsequently used as a stirrer to secure uniformity of temperature in that vicinity.

The water in the boiling tube is now slowly heated and kept constantly stirred by means of air introduced by a rubber blowing-bulb attached to a glass tube extending nearly to the bottom of the vessel. When the temperature of the alcohol-water mixture rises to about 6° below the m. p., the disc of fat begins to shrivel and gradually rolls up into an irregular mass. The thermometer is now lowered until the fat particle is even with the centre of the bulb, which should be small, so as to indicate only the temperature of the mixture near the fat. A gentle rotatory motion is given to the bulb, the temperature being meanwhile so regulated that the rise of the last 2° takes about 10 minutes. As soon as the mass of fat is seen to become practically spherical, the reading is taken, with the aid of a cathetometer or reading-glass.

The test-tube is now removed and replaced by a second one containing alcohol and water, and a new observation made with another disc of the fat, the temperature of the bath being now so regulated as to reach a maximum of about 1.5° above the m. p. of the substance. The new reading should be checked by a third observation, which should be in close agreement with the second result.

Solidification Point.

Dalican's Method.—The useful technical method, devised by Dalican in 1868 for the examination of fatty acids, is largely employed in commercial work in England and France under the name of the "*titer test.*" A test-tube, about 5 in. in length by 2/3 in. in diameter, is fitted with a ring or collar of cork or india-rubber, by which it is fixed in the mouth of an empty bottle or flask. The melted substance is then poured into the (warmed) tube till it is about 2/3 filled, and a delicate thermometer, previously warmed, is suspended freely in the liquid, so that the bulb may be wholly immersed. When the fat commences to solidify at the bottom of the tube, it is slowly stirred by giving the thermometer a circular movement first 3 times to the right and then 3 times to the left. At first the mercury falls, but subsequently rises to a point at which it remains stationary for about 2 minutes. This temperature is taken as the solidification point of the substance, and the results are very constant provided the same apparatus and method of working be employed.

Modification of Dalican's Method (Official in United States).—The following is the A. O. A. C. method: 25 grm. of the fat are saponified in a metal dish with 60 c.c. of 30% sodium hydroxide (36° B.) and 75 c.c. of 95% alcohol or 120 c.c. of water, and the mass evaporated to dryness. The dry soap is dissolved in 1,000 c.c. of boiling water, and the solution boiled for 40 minutes to expel all alcohol, and then treated with 100 c.c. of 30% sulphuric acid (25° B.) and heated until the fatty acids are clear. The fatty acids are then thoroughly washed, separated from the water, filtered through a dry filter and dried for 20 minutes at 100°.

The dried fatty acids are allowed to cool to 15° to 20° above the expected m. p., and poured into a test-tube 100 mm. in length by 25 mm. in diameter, which is fitted by means of a cork into a flask 150 mm. in height by 70 mm. in diameter. The thermometer graduated from 10° to 60° in tenths of a degree is passed through an opening in the cork of the tube, so that its bulb reaches to about the middle of the material. The 10° mark on the scale should be 3 to 4 cm. above the bulb and the entire length of the thermometer should be about 36 cm. The estimation should be made with the outside temperature about 10° lower than the solidification temperature. The readings should be made at short, preferably equal, intervals, and the maximum point reached in the short rise after the mercury ceases to fall is the solidification point or "titer." Duplicate observations should agree within 0.1.

Finkener's Method (Official for Customs Examination in Germany).

—This method is used in Germany for the technical differentiation of lard, tallow, and candle-fats. If the solidification point is below 30° it belongs to the first class; between 30° and 45°, to the second (tallows); and above 45°, to the third. Pressed tallow, however, may still pass as tallow even with a solidification point above 50°, provided it be declared as such and does not contain more than 50% of free fatty acids. In Finkener's method (*Chem. Zeit.*, 1896, **20**, 132) the fatty acids are dried as in Dalican's method and a larger quantity (150 grm.) introduced with a flask of prescribed dimensions up to a definite mark, the flask being then closed by means of a delicate thermometer on which is an expansion ground to fit the neck of the flask. The flask is then placed in a wooden box, in the top of which is an opening for the stem of the thermometer. The whole is allowed to stand and the readings taken at intervals of 2 minutes after the temperature has fallen to about 50°. The solidification point thus estimated is slightly higher than that given by the original Dalican method. This method offers no advantages over the ordinary method.

Wolfbauer's Method (used in Austria).—A test-tube 15 cm. long and 3.5 cm. in diameter is nearly filled with the melted fatty acids, and closed by means of a cork through which passes the thermometer. The tube is then fitted through an opening in the cork of a wide-mouthed bottle. The mass is stirred with the thermometer until it becomes turbid, and the readings then taken without further stirring (*Mitt. d. k. k. techn. Gew. Mus. in Wien.*, 1894, 57).

Shukoff's Method (used in Russia).—The melted fatty acids are introduced into a tube which is fitted into a bottle, as in Wolfbauer's method, though the dimensions are different. As soon as the temperature has fallen to within 5° above the expected solidification point, the apparatus is vigorously shaken from the top to the bottom, until the contents of the tube become turbid, the readings being then taken. Results thus obtained agree closely with those given by Wolfbauer's method. A vacuum-jacketed tube closed by means of a rubber cork was also employed by Shukoff, but his later apparatus mentioned above is more commonly used (*Chem. Rev. Fett. u. Harz. Ind.*, 1899, **6**, 11; *Chem. Zeit.*, 1901, **25**, 1111).

In comparing results obtained by the foregoing methods it has been found that the method and duration of saponification have no material influence, provided that the alcohol used is subsequently completely expelled, and that the fatty acids are thoroughly dried. Thus the solidification point of properly dried acids may be 0.6° above that of the same acids in which a trace of moisture has been left. The form of the apparatus has an influence when the quantity of fatty acids used is small, and cooling from outside proceeds too rapidly. Until an international method has been fixed, it is advisable in giving results to state the method by which they were obtained.

Temperature Tests.—The rise of temperature which ensues on treating a fixed oil with concentrated sulphuric or nitric acid, or bromine, is a measure of the extent and intensity of the chemical action which ensues. The use of sulphuric acid was originally proposed by Maumené (*Compt. rend.*, 1852, **35**, 572).

Maumené Test.—The following method of applying this test is recommended by Archbutt, and is in common use: 50 grm. of the oil are weighed into a 200 c.c. beaker, and the latter immersed in a capacious vessel of water, together with the bottle of strong sulphuric acid, until they are both at the same temperature, which should not be far from 20°. The beaker containing the oil is then wiped, and placed in a cotton-wool nest previously made for it in a cardboard drum, or a wider beaker. The immersed thermometer is then observed, and the temperature recorded. 10 c.c. of the concentrated sulphuric acid should then be withdrawn from the bottle with a pipette, and allowed to run into the oil. During the addition of the acid, which should occupy about 1 minute, the mixture must be constantly stirred with the thermometer, and the agitation continued till no further rise of temperature ensues. This point is readily observed, as the indication remains constant for a minute or two, and the temperature then begins to fall.

The results obtained from a particular oil are remarkably constant, when the acid is of a uniform strength and a defined method of manipulation is rigidly adhered to, but apparently insignificant differences in the mode of operation result in serious discrepancies in the results. Thus, Archbutt observed a rise of 78.5°, when the oil was stirred until all the acid was added and the thermometer then held stationary in the middle of the oil, but when the stirring was continued until no further rise of temperature was observed, the increase was only 73.5°.

When the temperature exceeds 60° it is impossible to obtain concordant results. Maumené, therefore, advocated diluting highly unsaturated oils, such as linseed or marine animal oil, with olive oil, so as to prevent charring of the mixture, whilst Ellis (*J. Soc. Chem. Ind.*, 1886, **5**, 161) recommended the use of mineral oil for the purpose.

Carbon tetrachloride, however, is preferable to either of these substances as a diluting agent, and Mitchell (*Analyst*, 1901, **26**, 169) has shown that, when the oil is diluted with that substance, the rise of temperature with unoxidised oils is, in most cases, proportional to the rise of temperature with bromine. This indicates that, under such conditions, the rise in temperature is probably due solely to absorption of the sulphuric acid by the unsaturated bonds.

	Rise of temperature with sulphuric acid; °				
	Maumené	Baynes	Dobb	Archbutt	Allen
Olive oil	42	40	39–43	41–45	41–43
Almond oil	52–54	35	....	....	....
Rape and Colza oils	57–58	60–92	54–60	55–64	51–60
Arachis oil	67	....	....	47–60	....
Beechnut oil	65	....	....	....	....
Sesame oil	68	....	....	65	....
Cottonseed oil; crude	....	84	61	70	67–69
Cottonseed oil; refined	....	77	....	75–76	74–75
Poppy seed oil	74	....	....	86–88	....
Nigerseed oil	....	82	....	....	81
Hempseed oil	98	....	....	....	....
Walnut oil	101	....	....	....	....
Linseed oil	103	104–124	....	....	104–111
Coconut olein	....	....	....	....	26–27
Castor oil	47	....	....	46	65
Lard oil	....	....	....	....	41
Tallow oil	41–44	....	....	....	....
Neatsfoot oil	....	....	....	43	....
Horsefoot oil	51	....	....	....	....
Whale oil; northern	....	....	....	....	91
Whale oil; southern	....	....	85–86	92	....
Porpoise oil	....	....	....	....	50
Seal oil	....	....	....	....	92
African fish oil	....	....	156	....	....
Shark-liver oil	....	....	....	....	90
Codliver oil	102–103	116	....	....	113
Skate-liver oil	102	....	....	....	....
Menhaden oil	....	....	....	123–128	126
Sperm oil	....	....	....	51	45–47
Bottlenose oil	....	....	....	42	41–47
Oleic acid	....	....	....	37·5	38·5

Owing to the notable difference in the rise of temperature caused by comparatively slight variations in the mode of operating, many of the recorded figures obtained by Maumené's test have little value. Hence it is desirable to compare a sample with one or more oils of known purity under exactly similar conditions. The figures in the table show the kind of result to be *expected* from various oils, but they must not be relied on too rigidly.

From these figures it will be seen that with some mixtures, for instance olive with cottonseed oil and rape with linseed oil, the rise of temperature with sulphuric acid may afford a means of forming an approximate estimate of the proportion of ingredients.

In order to obviate the effects of the use of different strengths of acid, Thomson and Ballantyne (*J. Soc. Chem. Ind.*, 1891, **10,** 233) ascertain the rise of temperature obtained on mixing 50 grm. of water with 10 c.c. of strong sulphuric acid and under precisely the same conditions as those used for testing the oil. The *specific temperature-reaction* of the oil is obtained by multiplying the rise of temperature of the oil-acid mixture by 100, and dividing by the rise of temperature of the water-acid mixture.

It is probable that the Maumené test will, ere long, be entirely displaced by more accurate methods, though it is still frequently employed as a rapid means of obtaining preliminary information.

The bromine thermal method devised by Hehner and Mitchell (*Analyst*, 1895, **20,** 146) is based upon the fact that the heat evolved on the addition of bromine to unsaturated fatty acids or glycerides is, as a rule, proportional to the degree of unsaturation. Thus, when once a relationship has been established between the iodine value of an ordinary unoxidised fat and its bromine thermal value obtained under standard conditions, the degree of unsaturation (*i. e.*, the iodine value) of similar fats may be rapidly ascertained.

1 grm. of, *e. g.*, lard, the iodine value of which has been accurately determined by Hübl or Wijs' method, is dissolved in 10 c.c. of chloroform or carbon tetrachloride in a small Dewar's vacuum-jacketed tube, and the temperature of the solution taken by means of a standard thermometer graduated in tenths of a degree. 1 c.c. of bromine is then introduced by means of Hehner and Mitchell's bromine pipette,[1] the

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[1] This consists of a 1 c.c. pipette, connected at the top with a tube bent twice at right angles and containing caustic lime kept in position by means of asbestos plugs. On applying suction to the end of this tube, all bromine vapour is retained by the lime.

mixture rapidly stirred with the thermometer, and the rise in temperature recorded.

The ratio between the values gives a factor (*e. g.*, 5.5), which, when multiplied by the rise of temperature observed under identical conditions with a similar fat or oil, gives a result in close agreement with the iodine value of the latter.

An apparatus thus standardised for lard gives good results with other animal body fats, with butter, and with most unoxidised vegetable oils and fats. It does not give concordant values, however, with Japanese wool (tung) oil, blown rapeseed oil, blown cottonseed oil and boiled linseed oil, evidently owing to substitution of the bromine taking place in these cases.

The value and limitations of the bromine thermal process are discussed by Jenkins (*J. Soc. Chem. Ind.*, 1897, **16**, 194) and by Archbutt (*ibid.*, 309), and modifications have been proposed by Wiley (*J. Amer. Chem. Soc.*, 1896, **18**, 378) and by Gill and Hatch (*ibid.*, 1899, **21**, 27). These modifications offer no advantage over the original method.

Solubilities of Fats and Fixed Oils.

Fats and oils are, without exception, insoluble in *water* and *aqueous liquids* generally.

In cold *alcohol* the fixed oils are, as a rule, but little soluble, and the solid fats and waxes still less so. In boiling alcohol, however, some of the fluid oils dissolve to a considerable extent, especially if the solvent is anhydrous. In many cases, statements as to the solubility can only be regarded as giving a rough indication of the amount of free fatty acids in the sample examined. Speaking generally, it may be stated: (1). That oils containing the esters of lower fatty acids (*e. g.*, porpoise oil, cocoanut oil, butter-fat) are exceptionally soluble in alcohol. (2). That oils containing the glycerides of linolenic and isolinolenic acids are fairly soluble. (3). That castor and croton oil are readily soluble in alcohol, and are sharply differentiated from most other oils by this characteristic.

Ether, chloroform, carbon tetrachloride, benzene, and oil of turpentine dissolve fixed oils readily, and are in many cases miscible with them in all proportions.

Petroleum spirit is also an excellent solvent for most oils and fats, though castor oil (*q. v.*) forms a striking exception, being practically insoluble in that liquid.

Valenta Test.—A method of distinguishing between different fats and oils was based by Valenta (*Dingler's polyt. J.*, 1884, **252**, 296) on the differences in their solubility in glacial acetic acid. A hot solution of the oil is gradually chilled and the temperature at which turbidity occurs recorded.

The incomplete solubility of rape oil and other oils from the *Cruciferæ*, even at the b. p. of acetic acid, is noteworthy, as are the low figures found for linseed oil, nigerseed oil, and menhaden oil, as compared with those for the non-drying oils.

The test is open to the objection that the slightest variations in the strength of acetic acid, and in the method of stirring and observing the turbidity point have the greatest influence upon the results.

To obtain comparable results, it is essential to follow invariably the same details of working, to use acids of exactly the same strength, and to see that the fat is free from water. The most accurate method of ascertaining the strength of glacial acetic acid is to ascertain its solidifying point, and to compare the results with the figures given by Rüdorff (*Pharm. J.*, 1871–2, [3], **2**, 241):

Glacial acetic acid containing water; %	Solidifying point; °
0.0	16.7
0.497	16.65
0.99	14.8
1.477	14.0
1.961	13.25

The modification of the method introduced by Chattaway, Pearmain and Moor (*Analyst*, 1894, **19**, 147) embodies the various precautions necessary for obtaining concordant results; but, at best, the method should only be regarded as a rapid preliminary sorting test, or as a confirmation of results obtained by other methods:

The mixture of 2.75 grm. of the fat and 3 c.c. of glacial acetic acid (99·5% strength) is heated in a stoppered tube about 10 cm. long by 1.25 cm. in diameter, which is immersed in hot water and shaken until a clear solution is obtained. It is then left in warm water with a thermometer attached to it until the contents become turbid. In the case of oils that have been excessively heated, no reliance can be placed upon the test. The following results were thus obtained:

Oil or fat	°	Oil or fat	°
Butter-fat (24)			
Highest	39.0	Seal oil (2)	65.0–70.0
Lowest	29.0	Japan fish oil (2)	47.5 and 19.0
Mean	36.0	Herring oil	90.0
Margarine (5)		Nigerseed oil	68.5
Highest	97.9	Sunflower oil (2)	59–62.5
Lowest	94.0	Bottlenose oil (2)	80.0–96.0
Mean	95.0	Lard oil (3)	75.0–76.0
Olive oil (10)	83.0–91.0	Lard (4)	97.0–98.0
Almond oil (5)	72–87.0	Neatsfoot oil	72.0
Cottonseed oil (7)	71–89.0	Rosin	56.0
Cod oil (3)	26.5–31.0	Jamba oil (3)	Above 100
Codliver oil (3)	72.0–76.0	Cabbage oil	Above 100
Colza (German)	83.0	Beef stearin	Above 100
Rape oil (4)	63.0–78.0	Lard stearin	Above 100
Peach-kernel oil	82.0	Castor oil	Not above 18
Earthnut oil (3)	72.0–73.5	Wool-grease olein	Not above 18
Linseed oil	46.0–52.0		

Criticisms and modifications of the Valenta test have been made by Hurst (*J. Soc. Chem. Ind.*, 1887, **6**, 22), Thomson and Ballantyne (*ibid.*, 1891, **10**, 233), and Jones (*Analyst*, 1894, **19**, 151). Its use in butter analysis is discussed in another section.

Critical Temperature of Solution.—A useful test for distinguishing between different fats and oils was devised by Crismer (*Bull. de l'Ass. belge. Chim.*, 1895–1896, **9**, 71, 143, 359). It is based upon the fact that when a substance is dissolved in, *e. g.*, alcohol under pressure, and the solution slowly cooled, the temperature at which the solid just begins to separate is fairly constant for one and the same kind of substance.

This point, the *critical temperature of solution*, stands in a certain sort of relationship to the amount of insoluble fatty acids in a fat, and in the case of mixture is approximately the arithmetical means of the values of its constituents.

It is ascertained as follows: A few drops of the melted and filtered substance are mixed with alcohol of known sp. gr. in a tube of a few mm. in diameter. This tube is then sealed up and attached by platinum wire to the bulb of a thermometer, which is immersed in a bath of sulphuric acid. The bath is slowly heated until the meniscus separating the layers of liquid appears a horizontal plane. The tube is then removed, turned sharply once or twice, to render its contents homogeneous, and replaced in the bath, which is now allowed to cool slowly, the thermometer and attached tube being meanwhile continually shaken, until a perceptible turbidity appears. This temperature is the critical temperature of solution. In this way the following results were obtained:

Substance	Critical temperature of solution	Substance	Critical temperature of solution
With 90% *alcohol*	°	*With alcohol of sp. gr.* 0.8195	°
Butter-fat	99–106		
Margarine	122–125	Mineral oils (various)	135.5–140
Arachis oil	123	Valve oil	197
Cottonseed oil	115.5	Animal oil	120
Sesame oil	120	Sheepsfoot oil	102
Olive oil	123	Lard oil	104
Almond oil	120	Neatsfoot oil	95
Rape oil (crude)	136	Colza oil	132–135
Rape oil (refined)	132.5	Japan fish oil	108
Hempseed oil	97	Butter-fat (10 samples)	95–100
Nut oil	100.5		
Castor oil	0		
Linseed oil (oxidised)	70		

Old and rancid butter-fat shows a lower value than fresh butter-fat, but after removal of the free fatty acids by treatment with sodium carbonate and washing the fat with hot water, normal values are obtained.

Crismer's figures for butter and margarine were in the main confirmed by Asboth (*Chem. Zeit.*, 1896, **20**, 685).

CLASSIFICATION OF FATS, OILS, AND WAXES.

In studying the characters of fixed oils, and identifying oils of unknown nature, valuable assistance is obtained from a suitable arrangement of the oils in classes or groups. The classification here adopted is based on a joint consideration of the origin, physical characters, and chemical constitution of the oils. An attempt is likewise made to classify the oils so that each group contains some important commercial oil which is typical of the other members of the group. Thus, the oils included respectively in the rape-oil, olive-oil, and cocoanut-oil groups present a more or less close resemblance to rape-oil, olive-oil, and cocoanut-oil, respectively.

I. **Olive-oil Group.**—*Vegetable Oleins.*—The oils of this group have a sp. gr. ranging from 0.911 to 0.923, and hence are, as a rule, lighter than the oils of Groups III, IV, and V. Their viscosity is notably greater than that of the drying oils, but inferior to that of rape oil, and they do not lose their power of producing a greasy stain on paper, however long they may be exposed to the air. They yield very solid products in the elaidin test, and are also characterised by their relatively low iodine values and medium saponification values. They contain olein as a main constituent, with smaller quantities of the glycerides of saturated fatty acids (palmitin, stearin, arachidin, etc.) and in some cases, at all events, of glycerides of more unsaturated fatty acids such as linolic acid. They yield no insoluble bromides on treatment with bromine, and their fatty acids yield, at most, only traces of linolic tetrabromide.

II. **Rape-oil Group.**—The oils in this group are derived from the *Cruciferæ.* They are classed as non-drying oils, though this characteristic is less pronounced than in the case of the oils in Group I, from which they may be distinguished by their low saponification values, and by forming a paste-like product in the elaidin reaction. Some of these oils resemble linseed oil in yielding an insoluble product on treatment with bromine, possibly the bromide of a mixed glyceride containing linolenic acid. Their low saponification values are probaby due to the presence of glycerides of erucic acid, $C_{22}H_{42}O_2$, whilst ralpic acid (isomeric with oleic acid) is present in rape oil.

III. **Cottonseed-oil Group.**—In sp. gr. these range from 0.9170 to 0.9290, the values of the crude oils being somewhat higher than those of the refined products. They are usually classified as *semi-drying oils* from the fact that they come between the non-drying oils and the drying oils, both in this respect and in their chemical composition. They have fairly high iodine values, and their fatty acids yield considerable amounts of linolic tetrabromide on treatment with bromine. In the elaidin test they yield soft solid masses, intermediate between the hard products given by the oils of Group I and the fluid products from the drying oils. They consist largely of linolin and olein, with smaller quantities of glycerides of solid fatty acids and traces of linolenin.

IV. **Linseed-oil Group.**—*Drying Oils.*—They range in sp. gr. from 0.9215 to 0.9430, and are thus distinctly heavier than the oils of the preceding groups. They are not solidified by treatment with nitrous acid, evolve great heat in the Maumené test, and have high iodine values. Linseed oil (and to a less extent some of the other oils) yields a large amount of an insoluble bromide on treatment with bromine. On exposure to the air in thin layers they absorb oxygen and form varnishes which are at first sticky, but subsequently become plastic or brittle. The viscosity of the drying oils is less than that of the preceding groups. In composition they differ from the semi-drying oils in containing a greater proportion of the glycerides of the highly unsaturated acids (linolenic and isolinolenic acids). The composition and properties of tung oil differ greatly from those of other members of this group.

V. **Castor-oil Group.**—The oils in this group have little in common, though some are characterised by their great viscosity and high sp. gr. Castor, curcas and croton oils have also the characteristic of ready solubility in alcohol and glacial acetic acid, and of marked purgative properties, but curcas oil is less soluble in alcohol than the others. In castor oil and grapeseed oil glycerides of a hydroxy-acid such as ricinoleic acid predominate, and are indicated by the high acetyl value of the oil. Croton oil has a high Reichert-Meissl value, due to the presence of glycerides of volatile fatty acids.

VI. **Cacao-butter Group.**—*Vegetable Fats.*—This group includes solid fats, consisting mainly of glycerides of higher fatty acids such as myristic, palmitic, stearic and oleic acids. They contain only small amounts of glycerides of volatile acids as is shown by the low Reichert-Meissl values. The fairly high iodine values point to the presence of a considerable proportion of glycerides of oleic and, probably, linolic acids.

VII. **Coconut-oil Group.**—*Vegetable Fats.*—The members of this group are fats of high sp. gr. and with low saponification values. They also include the two commercial vegetable "stearins" obtained from coconut and palmnut oils. The typical fats of the group (coconut and palmnut oils) contain a considerable amount of the glycerides of the lower fatty acids, whence their high Reichert-Meissl values. They are also distinguished from the fats of the preceding group by their high saponification values (indicating glycerides of lower fatty acids) and low iodine values (indicating the small proportion of unsaturated glycerides).

VIII. **Lard-oil Group.**—*Animal Oleins.*—In this group are included the oils, fluid at ordinary temperatures, which are obtained from terrestrial animals. They have lower iodine values than the corresponding vegetable non-drying oils (Group I), though they also yield more or less solid products in the elaidin test. They consist mainly of olein with smaller quantities of palmitin, stearin, and probably linolin.

IX. **Tallow Group.**—*Animal Fats.*—The tallow group comprises the fats from terrestrial animals, which are solid or semi-solid at the ordinary temperature. The body fats consist of stearin, palmitin, and olein with smaller amounts of linolin and other glycerides; whilst butter-fat is distinguished from the other members of the group by its high sp. gr., low saponification value, and high Reichert-Meissl value, due to the presence of a considerable amount of the glycerides of butyric and other lower fatty acids. Animal fats may be distinguished from vegetable fats by the phytosteryl acetate test (*q. v.*).

X. **Whale-oil Group.**—*Marine Animal Oils.*—This group comprises the majority of the fluid oils obtained from fish and marine mammals. They are distinguished as a class by their offensive fishy odour, which becomes more perceptible on warming; by the reddish-brown colour they assume when subjected to the action of chlorine; and by the reddish or reddish-brown colour produced on boiling them with a solution of caustic alkali. With concentrated sulphuric acid they give considerable rise of temperature and colorations, varying from light red to purple and brown. Most members of the group dry more or less on exposure to the air, and yield but little solid elaidin on treatment with nitrous acid. In these respects they resemble the vegetable oils of the cottonseed group, and have similar sp. gr. The oils from the sperm and bottlenose whales are peculiar, as regards physical characters and chemical constitution, and form a separate class (Group XI). "Train oil" includes the oil from the blubber of any marine mammal.

On treatment with bromine, many of the oils of this group yield an insoluble bromide, which may be distinguished from the similar product given by linseed and other drying oils by turning black when heated.

Porpoise oil is characterised by its high saponification value and high Reichert-Meissl value due to the presence of glycerides of valeric acid. The other oils in the group consist largely of glycerides of very unsaturated acids, some of which are isomeric with linolenic acid, and others still more unsaturated. Some of them, such as codliver and other liver oils, also contain a considerable amount of cholesterol and allied biliary products.

XI. **Sperm-oil Group.**—*Liquid Waxes.*—The members of this group differ from all the fatty oils of previous classes in consisting essentially of esters of the ethyl series. In this respect they resemble the true waxes, but are fluid at the ordinary temperature. They are of less sp. gr. than the true oils at the ordinary temperature and at the b. p. of water; and on saponification yield considerable proportions of solid higher homologues of ethyl alcohol. They do not dry or thicken notably on exposure to air and yield solid elaidins on treatment with nitrous acid.

XII. **Spermaceti Group.**—*Waxes.*—The members of this group are solid at ordinary temperatures, and more or less resemble beeswax, the prototype of the class. They consist essentially of esters of the higher radicles of the ethyl series, with in some cases an admixture of higher monatomic alcohols and higher fatty acids in the free state. Carnaüba wax seems also to contain diatomic alcohol radicles. Sperm and bottlenose oils (Table XI) resemble the waxes in constitution, but are liquid at ordinary temperatures. The substances known as Japan wax and myrtle wax (Table VII) are fats, not true waxes. Paraffin wax and mineral wax are hydrocarbons, and hence quite different in chemical constitution from the true waxes of animal and vegetable origin.

The following tables give the values likely to be obtained in the examination of the chief oils, fats, and waxes of commercial importance:

PROBABLE VALUES OF FRESH OILS BASED ON RECORDED FIGURES.

I. OLIVE OIL GROUP.

Oil	Sp. gr. at 15.5°	Solidification point °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value	Acetyl value
Almond	0.914–0.920	−10 to −20	13–14	188–192	0.5	96	93–100	....
Arachis (earthnut)	0.911–0.926	+ 3 to +10	27–30	186–194	0.5	95–96	83–101	....
Apricot-kernel	0.915–0.921	−14 to −20	3–5	188–193	....	....	100–109	....
Hazelnut	0.916–0.917	−10 to −20	20–25	191–197	0.9–1.0	95.5	83–90	....
Olive	0.914–0.920	Turbid at +2	21–30	185–196	1–0.3	....	77–95	10–11
Olive-kernel	0.918–0.920	....	....	182–184	....	....	87–88	....
Peach-kernel	0.918–0.923	below −20	10	191–193	....	....	92–99	....
Plum-kernel	0.912–0.920	−5 to −8	13–15	191–192	....	....	100	....
Tea seed	0.917–0.927	−5 to −12	....	190–194	....	91.5	88–90	....

II. RAPE OIL GROUP.

Oil	Sp. gr. at 15.5°	Solidification point °	M. p. of fatty acids	Saponification value	Reichert-Meissl value	Hehner value	Iodine value	Acetyl value
Black mustard seed	0.9155–0.9185	−17	16–17	173–175	....	96	104–120	....
Eruca sativa seed	0.915–0.918	....	....	169–174	0.1–0.8	95.5	97.5–99.5	....
Indian mustard seed	0.916–0.921	....	....	172–180	0.3–0.9	95.5	102–108	....
Jamba	0.915–0.916	−10 to −12	19–21	173–175	....	96.5	96–102	....
Radish seed	0.9163–0.9175	−10 to −17	20	174–178	0.3	96	93–96	....
Rape seed (colza)	0.914–0.916	−10	16–21	170–175	0.0–0.7	94.5–96.5	97–105	14.5
Ravison	0.917–0.922	−8	....	177–181	....	....	109–122	....
White mustard seed	0.914–0.916	−8 to −16	15–16	170–174	....	96–96.5	....	....

III. COTTONSEED OIL GROUP.

Oil	Sp. gr. at 15.5°	Solidification point °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value	Acetyl value
Beechnut	0.9220–0.9275	−17	23	191–196	....	95–96	104–111	....
Brazil-nut	0.9170–0.9180	0 to +3	28–30	193–194	....	....	95–106	....
Cameline	0.920–0.9270	−18	13–14	188	....	....	135–152	....
Cottonseed	0.9130–0.930	0 to −1	34–40	191–196	0.7–0.9	95–96	104–116	21–25
Cress seed	0.920–0.9240	−15	16–18	180–183	0.2–0.4	95.5	102–118	....
Madia	0.923–0.9286	−10 to −20	23–26	193	....	....	121	....
Maize	0.9213–0.9268	−10 to −12	17–22	186–193	4–4.5	93	115–128	11–11.5
Pumpkin seed	0.9200–0.9250	−15	26–28	188–193	....	96	121–130	....
Sesame	0.9210–0.9240	−4 to −6	24–32	188–193	1–2	95–96	103–117	....
Soja bean	0.9240–0.9270	+8 to 15	27–29	191–193	....	95.5	121–124	....
Wheat	0.9240–0.9290	semi-solid at 0	39–40	183–190	2–3	....	115	....

IV. LINSEED OIL GROUP.

Oil	Sp. gr. at 15.5°	Solidification point °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value	Acetyl value
Candlenut	0.920–0.9260	below −18	20–21	189–195	1–2	95–96	153–164	10
Cedarnut	0.930–0.9320	−20	11–12	192	2.0	92–93	150–159	....
Hempseed	0.928–0.9330	−15 to −28	17–28	190–195	....	....	145–166	....
Lallemantia	0.9336	−35	22	185	1.5	93.5	162	....
Linseed	0.9315–0.9410	−16 to −27	17–24	190–201	0	95–95.5	175–201	....
Nigerseed	0.9248–0.9280	−8	25	186–192	0.11–0.63	95.5	126–134	....
Pinenut	0.9215–0.9250	−18 to −20	16–19	191–193	....	....	106–120	....
Poppy	0.9240–0.9260	−15 to −20	20	193–195	0.0	95.5	153–158 (?)	....
Safflower	0.9251–0.9280	....	....	187–194	0	95.5	130–149	16.1
Sunflower	0.9240–0.9260	below −17	22–24	188–193	....	....	123–136	....
Tung	0.9360–9430	+2 to +3 [after keeping, below −17]	30–49	191–196	....	96–96.5	155–166	....
Walnut (nut)	0.9240–0.9268	−12 to −24	15–20	190–197	0.0	94–94.5	139–148	....

V. CASTOR OIL GROUP.

Oil	Sp. gr. at 15°	Solidification point °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value	Acetyl value
Castor	0.960–0.967	−17 to −18	13	175–183	2.5	....	84–85	150
Croton	0.9426–0.9437	−8 to −18	17–19	205–215	12–13.5	88–90	102–109	20–39
Curcas	0.9190–0.924	+30	24–30	193–210	0.2–0.4	95.2	98–110	14–25
Grape seed	0.9350	−10 to −13	23–25	178–179	0.45	92.0	94–96	144.5

VI. CACAO BUTTER GROUP.

Fat	Sp. gr.	M. p. °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value
Bassia tallow (Mixture of Mohwah and Mahua butters)	0.9175 at 15° 0.8943 to 0.8981 at 100°	25–42	39.5–45	187–194	0.5–0.8	94.5–95	54–68
Borneo tallow	0.892 at 100°	37.5	53.5	192.4–196	....	....	30–31
Cacao butter	0.964–0.974 at 15° 0.8577 at 98°	30–34	48–53	192–195	0.2–0.9	....	32–42
Chinese tallow	0.9180 to 0.9217 at 15°	36–46	39–57	179–203	0.2	....	23–38
Cotton oil stearin	0.867 at 100°	30–40	27–45	194.5	....	96.5	89–93
Goa butter (Kokum butter)	0.911 at 50° 0.8889 at 100°	41–43	61.0	187–191.5	0.1–1.5	93.5–95.5	25–34
Laurel oil	0.8806 at 98.5/11.5	32–36	....	198–199	1.6	....	68–80
Mafura tallow	0.902 at 40°/15°	29–40	51–55	201–221	1.5	....	43.5–56
Nutmeg butter	0.945–0.996 at 15°	43–51	42.5	154–161	1–4.2	....	48–85
Palm oil	0.9210–0.9245 at 15°	27–43	48–50	200–205	0.8–1.9	94.5–97	53–58
Phulwara butter (Karité fat)	0.8970 at 100°/100	39	....	191	0.4	95	42
Piney tallow (Malabar tallow)	0.915 at 15° 0.8900 at 100°	36–42	56	189–191	0.2–0.4	....	38–39
Shea butter (Galam butter)	0.9175 at 15° 0.859 at 99.5°/15.5°	23–28	39.5–56	179–192	....	94.8	56–67

VII. COCONUT OIL GROUP.

Fat	Sp. gr.	M. p. °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value
Coconut oil	0.9259 at 15°	20–28	24–25	246–262	6.6–8.4	82.5–90.5	8.2–9.5
(Coconut oil)	0.8736 at 100°						
Coconut "stearin"	0.8700 at 100°	29.3–29.5	28.1	252	3.4	......	4.0–4.5
Japan wax	0.984 to 0.993 at 15.5°	50.4–56	56 to 62	214–237.5	......	90–90.5	4.2–15
Macassar oil	0.924 to 0.942 at 15°	22–28	52–55	213–230	9	91–91.5	48–55
Myrtle wax	0.875 at 98–99/15.5°	40–88	47.5	206–217	0.5	......	1.9–3.9
Palm-nut (Palm kernel) oil	0.8731 at 99°/15.5	23–30	21–28.5	243–255	5 to 6.8	91–91.5	10.5 to 17.5
Palm-nut "stearin"	0.8700 at 100°	31.5–32	28.5–29.5	242	2.2	......	8

VIII. LARD OIL GROUP.

Oil	Sp. gr. at 15.5°	Solidification point °	M. p. of fatty acids °	Sapon. value	Hehner value	Iodine value
Lard oil	0.913–0.919	−4 to + 10	33–38.5	193–198	97	67–82
Neatsfoot	0.914–0.916	0 to + 10	29–31	193–200	94.5–95.9	66–74
Tallow oil	0.916	0 to + 6	......	193–200	......	60–78

Horsefoot and sheepsfoot oil not included since usually sold as neatsfoot oil. Reichert-Meissl value for neatsfoot oil, 0.9–1.2.

IX. TALLOW GROUP.

	Sp. gr. at 15.5°	Sp. gr. at 98–100°	M. p. °	Solidification point °	M. p. of fatty acids °	Sap. value	Reichert-Meissl value	Hehner value	Iodine value
Beef fat	0.8950	0.8626	42–50	31–38	41–47.5	196	0.3–0.5	96–96.5	36–42
Bone fat	......	......	......	......	......	196.3	......	......	52.0
Butter fat	0.909–0.913 at 38.5°	......	28–36	......	38–42	215.8–241.1	21.0–33.4	85–89.5	28–42
Horse fat	0.916–0.922	......	35–43	......	31–54	195–199.5	0.3	94.5–97.5	76–86
Lard	......	0.8600	30–44	27–30	37–47	195–203	0.2	93–95	47.5–64
Mutton fat	0.937–0.953	......	47–49	......	34–36	196	0.3	95	33–50
Tallow	0.925–0.940	......	38–50	34–46	41–49	193–198	0.2	95–96	33–48

X. WHALE OIL GROUP.

Oil	Sp. gr. at 15.5°	Solidification point °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value
Codliver	0.922 to 0.930	−3	21–25	179–190	0.2	95.5	154–170
Menhaden	0.925 to 0.931	−4	....	189–193	1.0	....	139–174
Porpoise	0.926	....	....	203–253	46–56	68–72	30–125
Sardine	0.928–0.933	....	....	189–193	....	94.5	192–193 (Japanese sardine oil, 181–188)
Seal	0.924–0.9270	deposit at +3	22–23	190–193	0.2	93–96	130–152
Shark	0.916–0.9190	....	21–22	157–164	....	87–97	115–139
Whale	0.917–0.9237	....	14–18	184–194	0.7–2.0	93.5–96.5	116–128

XI. SPERM OIL GROUP.

Oil	Sp. gr. at 15.5°	Solidification point °	M. p. of fatty acids °	Saponification value	Reichert-Meissl value	Hehner value	Iodine value	Acetyl value
Bottlenose (Doegling)	0.876 to 0.881	....	10.5	123–130	1.4	....	80–85	....
Dolphin	0.918–0.922	deposit at −5	....	198	5–6	93	99.5	....
Sperm	0.878 to 0.884	....	13–14	120–137	1.3	....	80–84	4.4–6.4

XII. BEESWAX GROUP. WAXES.

Wax	Sp. gr. at 15.5°	Sp. gr. at 98°–99°	M. p. °	Acid value	Sap. value	Iodine value	Acetyl value
Beeswax	0.959–0.970	0.818 to 0.827	62–66	17–22	88–98	8.5–11.5	15.2
usually	0.962–0.966						
Carnauba wax	0.995–1.000	0.842 to 0.850	83–86	4–8	79–84	13.5	55.2
Chinese insect wax	....	0.809 to 0.811	81–83	....	80–93	....	....
Spermaceti	0.942 to 0.946	0.808 to 0.816	42–49	0.0–1.8	126–134.5	3–4	2.6
Wool fat	0.970–0.973	....	39–42	....	82–130	17–52	....
(Lanoline)	0.973	....	36–43	0.6–2.8	81–102	10–31	108–122

EXAMINATION OF FATS AND CRUDE OILS FOR FOREIGN MATTERS.

The term "foreign matters" used in this connection indicates substances added to the oils, such as rosin, soaps, hydrocarbon, water and mineral matter as well as excess of free fatty acids, but does not apply to substances which are natural constituents of an oil such as colouring matters, cholesterol, albuminous substances or chlorophyll.

The estimation of water, curd, and salt in fats such as butter and margarine is described in the special section dealing with butter. An oil, if clear, may be regarded as free from such extraneous matters, and their presence in a fat may usually be detected by melting the sample. If an opaque or opalescent oil result, or one containing visible particles of suspended matter or globules of water, it should be purified from these by filtration through dry paper before proceeding to search for rosin, fatty acids, soap, or hydrocarbons.

Soap is sometimes directly added to an oil, but its presence is more frequently due to the use of alkali employed to increase sp. gr. and viscosity. Soap is readily detected by dissolving the oil in about 3 times its volume of ether or carbon tetrachloride, adding a little water, and agitating the whole thoroughly in a separating funnel. The soap will dissolve in the water, while the other foreign matters will dissolve with the oil, in the ether or carbon tetrachloride, and may be recovered therefrom by distillation. The soap may be estimated by evaporating the aqueous liquid and weighing the residue after drying at 100°. The proportion of soap may also be inferred from the amount of carbonate left after igniting the oil.

Insoluble soaps are not infrequently present in oils, waste greases, and pharmaceutical preparations ("oleates"). Though insoluble in water, many of them are soluble in ether or petroleum spirit. They may be decomposed by agitating the mixture with dilute sulphuric acid, when the acid liquid will contain the metal of the soap, and a corresponding quantity of fatty acid will dissolve in the oily layer. When it is desired to ascertain the proportion of free fatty acids originally present in the oil, a titration with alkali should be made both before and after shaking with dilute acid. The difference between the two estimations represents the fatty acid liberated by the treatment.

Free Acid in Oils.—Commercial oils and fats very frequently contain notable proportions of free acid, which may either be mineral acid, as a result of incomplete separation after refining, or free fatty acid resulting from unskilful refining or from the natural decomposition of the oil.

Mineral acids are only accidentally present in fixed oils, and usually in very small proportions. Even minute quantities are highly objectionable in oil intended for lubricating, but are harmless when the article is to be used for soap-making. Mineral acids may be readily recognised by agitating the oil with warm water, separating the aqueous liquid, and testing it with a solution of methyl-orange, which will give an orange or red colouration if any mineral acid be present. The nature of the mineral acid, which is most commonly sulphuric, can then be ascertained by testing the aqueous liquid with barium chloride, silver nitrate, and other appropriate reagents. Oils which, from over-treatment with acid during refining, contain a sulphonated fatty acid, must be boiled with water for some time, in order to decompose the compound.

Free fatty acids are often normally present, and in some oils (*e. g.*, olive and palm) may exist in very large proportion. Free oleic acid is largely used as a lubricant in wool-spinning, and free palmitic and stearic acids are employed for making candles and night-lights. All are used for soap-making. Their proportion is estimated as described in the section (page 9) dealing with the *Acid Value.*

Rosin acids present in the sample will be estimated by the above process as fatty acids. Their separation from the latter is described below. *Mineral acids* will affect the accuracy of the results unless an allowance is made for them or they are previously separated by repeatedly agitating the oil with water. *Soap* and *hydrocarbons* do not interfere with the estimation.

The estimation of the acid value may be supplemented by a gravimetric estimation. The resultant alcoholic liquid is separated from the oil, the alcohol evaporated, and water added. This solution is agitated with a little petroleum spirit (not ether) to dissolve suspended oil, the aqueous liquid separated, and the fatty acid liberated from the soap solution by adding dilute sulphuric acid. On agitating with ether, separating the ethereal solution, and evaporating it to dryness, the fatty acids can be weighed. This method should be used when rosin acids may be present. In their absence, the estimation should be fairly concordant with the result of the titration. *Soap* should be previously separated. *Mineral acids* and *hydrocarbons* do not interfere with the results.

Rosin.—Common *rosin* or *colophony*, which is described in a special section, is added to oils to impart certain properties, but its employment often renders them wholly unsuitable for their intended purposes.

One of the methods of detecting rosin is by the brown colour it imparts to sodium hydroxide. The original sample is saponified, the alcohol boiled off, and the liquid treated with sufficient sodium hydroxide solution to cause precipitation of the soap. The solution, separated from the soap by decantation or filtration through glass-wool, will be dark brown if rosin is present. The same method serves for the recognition of rosin in soap, previous saponification being unnecessary. The method may also be applied to the mixture of fatty and resin acids separated in the manner described in the table on page 22. The dissolved rosin may be recovered by acidifying the alkaline liquid with hydrochloric acid, when a precipitate of resinous odour will be formed. The rosin may be isolated by agitating the liquid with ether and evaporating the ethereal layer to dryness, and may be identified by its physical and other characteristics.

In the absence of free fatty acids, rosin may be isolated from fixed oils by agitating the sample with moderately strong alcohol, separating the solution and evaporating it to dryness. It may also be isolated, and approximately estimated, by titrating the alcoholic solution of the sample with alkali and phenolphthaleïn as described elsewhere. As the several acids which ordinary colophony contains are not present in constant proportion, the neutralising power of rosin is variable, ranging from 0.310 to 0.430 grm. of colophony for 1 c.c. of N/1 alkali. The rosin subsequently extracted from the acidified aqueous liquid, and left on evaporating the ethereal solution to dryness, is readily recognisable by the taste and smell on heating, and often shows the physical characteristics of rosin.

In the last method of operating, the rosin is obtained in admixture with any free fatty acids the sample may have contained. These modify the physical properties of the extracted rosin very materially, and render the method useless for quantitative purposes. In such cases, if there is sufficient material for the purpose, a good indication of the relative proportions of fatty and rosin acids in the mixture may be obtained by observing the sp. gr. at the temperature of boiling water, as described on page 48. As, however, rosin varies considerably in sp. gr. and the fatty acids from various oils exhibit similar variations, the method furnishes but very rough results unless the source of the fatty acids be definitely known.

Estimation of Rosin Acids.—The most satisfactory method of separating rosin acids from fatty acids is that of Twitchell (*J. Soc. Chem. Ind.*, 1891, **10**, 804) which yields much more accurate results than other methods. It is based upon the fact that aliphatic acids are converted into ethyl esters when acted upon by hydrochloric acid gas in their alcoholic solution; whereas colophony undergoes little or no change under the treatment, abietic acid separating from the solution.

The rosin gives an acid indication in alcoholic solution with phenolphthaleïn, and interacts readily with potassium hydroxide to form a soluble soap. All that is necessary, therefore, is to make the fatty acids interact with alcohol and to titrate the rosin acids with standard alkali; or they may be treated with potassium hydroxide and the resulting rosin soap separated from the saponified fatty esters by means of petroleum spirit.

(*a*). *Gravimetric Method.*—From 2 to 3 grm. of the mixture of fatty acids and rosin are dissolved in 10 times their volume of absolute alcohol in a flask, and dry hydrochloric acid introduced in a moderate stream. The flask is set in a vessel with water to keep it cool. The acid is rapidly absorbed, and, after about 45 minutes, the esters separate, floating in the solution, and no more hydrochloric acid is absorbed. The current of gas is now stopped, and the flask allowed to stand for half an hour to complete the reaction. The liquid is diluted with about 5 times its volume of water and boiled until the acid solution is clear, the esters, with resin in solution, floating on the top. To this is added some petroleum spirit, and the whole transferred to a separating funnel, the flask being washed out with petroleum spirit. The acid solution is then run off, and the petroleum-spirit solution (which ought to measure about 50 c.c.) washed once with water and then shaken in the funnel with a solution of 0.5 grm. potassium hydroxide and 5 c.c. of alcohol in 50 c.c. of water. The rosin is immediately saponified and the two layers completely separated. The solution of rosin soap can then be run off, treated with acid, the rosin collected in any manner desired, dried, and weighed. A second washing of the soap with petroleum spirit is hardly necessary, as very little remains after the first extraction.

(*b*). *Volumetric Method.*—The first stages of the volumetric method are similar to the gravimetric, with the exception that the contents of the flask are washed into the separating funnel with ether instead of petroleum spirit, and the ethereal solution in the funnel is then thoroughly washed with water until the wash-water is no longer acid; 50 c.c. of alcohol, previously neutralised, are then added and the solution titrated with standard sodium hydroxide solution with phenolphthaleïn as indicator. If the combining equivalent of rosin is known, its percentage may be calculated, or some of the original mixture may be also titrated, when the difference in sodium hydroxide required will correspond to the fatty acids converted into esters.

The average combining equivalent of the samples of rosin examined by Twitchell was 346, and a closely similar value was found by Lewkowitsch (*J. Soc. Chem. Ind.*, 1893, **12,** 504). Hence an approximately correct result for the amount of rosin may be obtained by multiplying the number of c.c. of N/1 alkali used in the titration by 0.346. Certain varieties of commercial rosin, however, have combining equivalents differing very considerably from this average value. The results of test experiments have shown that in practice the volumetric figures though usually too high, are more accurate than the gravimetric figures, which are usually too low. A critical examination of this method was made by Lewkowitsch (*loc. cit.*)

Hydrocarbons.

The hydrocarbons most commonly added to fatty oils are:

1. Those produced from *petroleum* and by the distillation of *bituminous shale.*

2. Those produced by the distillation of common *rosin*, having the nature and properties detailed in the section on "Rosin Oil."

3. Neutral *coal oil;* being the portion of the products of the distillation of coal-tar boiling above 170°, and freed from phenolic bodies by treatment with soda.

4. Solid *paraffine*, employed for the adulteration of beeswax and spermaceti, and used in admixture with stearic acid for making candles.

Detection of Hydrocarbons.—The presence of hydrocarbons in fats and fatty oils is *detected* by the altered sp. gr. of the sample, which is decreased by members of the first class, and increased by rosin and coal-tar products; by the lowering of the flashing and b. p.; by the fluorescence of members of the first two classes; and by the incomplete saponification by alkalies. The taste and odour on heating are also valuable indications.

Sp. gr. is a character of some little value for detecting and approximately estimating hydrocarbons, but in practice the indications obtained are apt to be rendered valueless by the employment of a *mixture* which has the same sp. gr. as the oil to be adulterated.

The tendency of a hydrocarbon is to reduce the flashing and boiling points of the fixed oil, and in some cases a distinct separation may be effected by fractional distillation.

Fluorescence is a character of considerable value for detecting the presence of hydrocarbons. If undoubtedly fluorescent, the sample certainly contains some hydrocarbon, but the converse is not strictly true, as the fluorescence of some varieties can be destroyed by treatment, and some hydrocarbons have no fluorescence.

The best method of observing fluorescence is to make a thick streak of the oil on a piece of black marble, or glass smoked at the back, and to place the streaked surface in a horizontal position in front of, and at right angles to, a well-lighted window.

Most of the hydrocarbons employed for lubricating purposes are strongly fluorescent, and many others become so on treatment with an equal measure of strong sulphuric acid. A hydrocarbon possessing strong fluorescence may be evident in presence of a very large proportion of fixed oil; but if any doubt exist, the hydrocarbon should be isolated in the manner described below.

Estimation of Hydrocarbons.—The following method is based on saponification of the oil or fat, and extraction of the hydrocarbons from the aqueous solution of the soap by means of a suitable solvent such as ether: 5 grm. of the sample are saponified by alcoholic alkali, the solution freed from alcohol, and transferred to a separator of about 200 c.c. capacity, furnished with a tap below and a stopper at the top. The tube below the tap should be ground or filed off obliquely, so as to prevent any liquid from remaining in it. The liquid is diluted with water till it measures from 70 to 100 c.c. From 50 to 60 c.c. of ether should next be added, the stopper inserted, and the liquids thoroughly shaken and allowed to rest for a few minutes. As a rule, two well-defined layers will form, the lower one brownish, consisting of the aqueous solution of soap, the upper of ether, containing any hydrocarbon in solution. The addition of a few c.c. of alcohol will facilitate the separation when it does not readily occur.

The aqueous liquid is drawn off through the tap into a beaker. About 10 c.c. of water and a few drops of caustic alkali solution are added to the ether which remains in the separator, and the whole agitated. The washings are then run off in their turn, and after repeating the treatment with water, which is removed by the tap as before, the ethereal solution is poured off through the mouth into a weighed flask. The aqueous liquid and washings are then returned to the separator, and agitated with a fresh quantity of ether, which is washed and poured into the flask as before.

The agitation of the soap solution is repeated once more, to complete the extraction of the hydrocarbon oil. The ethereal solution will usually be strongly fluorescent. The flask containing it is attached to a condensing arrangement, and the greater part of the ether distilled off by immersing the flask in boiling water. When distillation has ceased, the condenser is detached and the flask placed on the top of the water-oven to eliminate the rest of the ether. Sometimes the hydrocarbon will contain globules of water; in this case the flask should be held horizontally, and rotated rapidly, so as to spread the oil over the sides in a very thin layer, and facilitate the evaporation of the water. When no more water is visible, and the smell of ether is scarcely perceptible, the flask is placed on its side in the water-oven for 10 or 15 minutes and weighed,[1] when the increase of weight over the original tare gives the amount of hydrocarbon oil extracted. Prolonged heating should be avoided, as many hydrocarbons are appreciably volatile at 100°. This is notably the case with coal-tar oil, and hence, in analysing mixtures containing it, the heating in the water-oven should be wholly dispensed with. With rosin oil, paraffin wax, and the denser mineral oils there is but little danger of loss by volatilisation at 100°.

The results obtained are correct to within about 1% in all ordinary cases.[2] Where extreme accuracy is desired, it is necessary to remember that most, if not all, animal and vegetable oils contain traces of matter wholly unacted on by alkalies. In certain cases, *e.g.*, butter-fat and cod-liver oil, this consists largely of cholesterol, $C_{26}H_{44}O$, which may be obtained in characteristic crystalline tablets by warming the ethereal extract with alcohol, and allowing the solution to cool. The proportion of unsaponifiable matter soluble in ether which is naturally present in fixed oils and fats, rarely exceeds 1.5 and is usually much less. Sperm and bottle-nose whale oils, however, constitute an exception, yielding about 38 to 40% of matter soluble in ether.

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[1] Sometimes it is very difficult to obtain a constant weight by the means indicated in the text. In such cases, instead of heating the flask on the water-oven, it should be kept on the bath of boiling water and a moderate current of air, filtered by passing it through a tube containing cotton-wood, should be blown through it by a second tube passing through the cork. The fittings are then detached, and the flask heated for a short time in the water-oven.

[2] Traces of fatty oils which had escaped saponification and traces of soap are apt to pass into the ethereal solution, and hence the proportion of unsaponifiable matter found is often slightly reduced on treating the ether-residue with alcoholic potassium hydroxide solution, and again extracting the solution of the soap with either.

Spermaceti and the other waxes yield after saponification large percentages of matter to ether, and hence the process is not available for the estimation of paraffin wax in admixture with these bodies, though it gives accurate results with the mixtures of paraffin and stearic acid so largely employed for making candles.

The following table indicates the behaviour of the constituents of complex mixtures of fats, oils, and waxes, when the aqueous solution of the saponified substance is shaken with ether:

Dissolved by the ether	Remaining in the aqueous liquid	
Hydrocarbon oils; including	Fatty acids.	In the form of potassium salts.
Shale and petroleum oils,		
Rosin oil hydrocarbons,	Rosin acids.	
Coal-tar oil,		
Paraffin wax and ozokerite,	Phenol,	
Vaseline.	Cresols,	
Neutral resins.	and other phenols.	
Unsaponified fat or oil.		
Unsaponifiable matter, as cholesterol from liver oils, etc.	Glycerol (glycerine).	
Dodecyl alcohol, from sperm and bottlenose oils.		
Cetyl alcohol, from spermaceti.	Excess of potassium hydroxide.	
Myricyl alcohol, from beeswax.		
Colouring matters, as from palm oil.		

The hydrocarbon having been isolated by saponifying the sample and agitating with ether, its nature may be ascertained by observing its sp. gr., taste, and smell, and behaviour with acids and bromine. If the proportion be small, it may be necessary to operate on a larger quantity than 5 grm. of the sample. A good approximation of the sp. gr. of the extracted hydrocarbons may be made on Hager's principle, by adding a drop of the oil to very dilute alcohol, or ammonia, and adjusting the strength of the liquid so that it may be identical with that of the drop of oil (see p. 48). The sp. gr. of the dilute alcohol is then ascertained in the usual way. The fluorescence of hydrocarbons is best observed in the manner described on page 79. It often becomes intensified by treating the extracted hydrocarbon with an equal volume of strong sulphuric acid.

The odour and taste of the hydrocarbons are often highly characteristic of their origin. The smell of coal-tar oil is readily observed; and the taste, especially the after-taste, of rosin oil is not to be mistaken. The smell produced on strongly heating a drop of the oil in a platinum capsule is also highly characteristic. Further details respecting the tests for hydrocarbons are given in the section on "Mineral Lubricating Oils."

The *higher alcohols* from sperm and bottlenose oil may be separated from hydrocarbons by treating the ether-residue with rectified spirit, which dissolves the alcohols without materially affecting the hydrocarbons.

If the aqueous liquid separated from the ethereal layer be treated with dilute sulphuric acid, the fatty acids are liberated, and may be weighed, titrated with standard alkali, or otherwise examined.

When it is merely desired to ascertain approximately the proportion of hydrocarbon oil in a mixture, and not to isolate it and examine it further, there is no occasion to extract the solution of the saponified oil with ether. Instead, the aqueous liquid may be at once acidified with dilute sulphuric acid, a little ether added to promote the separation of the mixed hydrocarbon oils and fatty acids, the aqueous liquid drawn off, and the oily layer repeatedly agitated with water till the washings are no longer acid to litmus. Rectified spirit and a few drops of phenolphthaleïn solution are then added, and the liquid titrated with N/10 alkali.

The amount of acid, calculated as oleic acid, multiplied by 1.053 gives the amount of saponifiable substances, and the difference may be regarded as unsaponifiable matter.

The latter represents the hydrocarbons, and the former the fat or fixed oil of the mixture, provided that waxes, including sperm and bottlenose oils, are absent.

When the nature of the fat or oil is known, and it is merely desired to estimate the proportion of hydrocarbon present, and not to ascertain its exact character, a very fair approximation to the truth can be obtained by ascertaining the saponification-equivalent of the sample.

The table on page 82 gives an outline of the processes described in the foregoing section.

EXAMINATION OF OILS CONTAINING FOREIGN ADMIXTURES

From 5 to 10 grm. of the sample (previously melted by warming if necessary) are passed through a dry filter, unless already perfectly clear.

Residue may contain *curd, salt, water, sand*, and *insoluble matters* generally. It may be washed with ether, dried, and weighed; then ignited gently and weighed again, the loss being the *volatile matter*, mostly organic.

The **Clear oil.** (N. B.—If an aliquot portion of the clarified oil is not blackened when shaken with alcohol and ammonium sulphide, and leaves no notable ash on ignition, thus proving the absence of metallic compounds, the following treatments with water and dilute H_2SO_4 may be advantageously omitted. The clear oil is agitated in a separating funnel with water and ether. The aqueous solution is separated, and the oil solution again shaken with ether if the previous treatment was found to remove anything.

Aqueous liquid contains *soaps of the alkali metals*. It is evaporated to dryness at 100°, and the residue weighed and further examined if desired. The *alkali* may be titrated with H_2SO_4 and Methyl Orange, and the characteristics of the liberated fatty acids determined.

Oil solution. Agitate with dilute H_2SO_4 and separate. Wash residual oil repeatedly by agitation with water till the aqueous liquid no longer reddens litmus.

Acid liquid may contain sulphates of metals previously existent as soaps. Also *boric acid* from linseed oil driers, and *phosphoric acid* from bone fat.

Solution of oil in ether. Add a few drops of phenolphthaleïn solution. Then add gradually, with repeated shaking, a solution of 2 grm. of NaOH in 10 c.c. methylated spirit and 90 c.c. of water, in quantity somewhat greater than is sufficient to produce a permanent red color. Then separate the undissolved oil without delay. Agitate the oil and aqueous liquid respectively with slightly alkaline water and with ether, and add the washings to the main quantities.

Aqueous liquid. Add Methyl Orange and then dilute H_2SO_4 till acid reaction is obtained. Then add as much more dilute H_2SO_4, so as to convert alkali into $KHSO_4$. Agitate or wash separated fatty acids with boiling water.

Oil. Evaporate off ether and saponify residual oil by alcoholic KOH. Boil off alcohol, dissolve soap in warm water, and agitate cooled solution with ether. Separate and agitate aqueous liquid a second and third time with ether. (In analysis of waxes, treatment of the dry soap with boiling toluene should be substituted for agitation of the solution with ether.)

Oily layer consists of *insoluble fatty and rosin acids*, free in original sample or as soaps of Al or heavy metals. Collect by help of ether, evaporate, weigh, and further examine.

Aqueous liquid. Distil to small bulk, titrating distillate with barium hydroxide; then evaporate and weigh barium salts of *volatile fatty acids*. *Non-volatile soluble acids* in retort leave Na_2CO_3 when neutralised by NaOH and evaporated and ignited.

Aqueous liquid contains *glycerol* and *soap*, formed by saponification of fixed oil of sample. Treated with dilute HCl, the weight of fatty acids obtained, multiplied by 1.055, gives approximately *neutral fixed oil* of sample. Glycerol may be determined in half of aqueous liquid.

Ethereal liquid evaporated at 100° leaves a residue which is weighed, and may contain *hydrocarbons, cholesterol, phytosterol, higher alcohols*, and *colouring matters*.

IDENTIFICATION OF FATS AND FIXED OILS.

The recognition of an unmixed fat or fixed oil may usually be effected by a careful application of the methods of examination already described. Systematic schemes for the purpose have been devised, but cannot be implicitly relied on, owing to the variable nature of the substances themselves. Most of the colour tests are of little value, unless confirmed by other indications.

In examining fats and oils for the detection of adulteration, the relative commercial value of the different kinds should be kept in view. In addition to the adulteration of the more valuable substances with the cheaper, the use of hydrocarbons derived from the distillation of petroleum, shale, coal, and rosin, is also extensively practised.

In practice it is often of less importance to know the origin of a sample than whether it may be used as a substitute for the genuine oil. This may be ascertained with tolerable certainty, and, in some cases, the nature of the adulterants may be definitely detected.

By the following systematic method identification may generally be effected, and much information gained that will suggest the special tests, for the substances suspected to be present:

1. Place a drop of the oil on the back of the tongue by means of a glass rod and taste it carefully, avoiding too hasty a decision. In this manner, marine animal oils, linseed, croton, mineral, rosin, and some other oils may often be detected. Rosin oil is remarkable for the nauseous after-taste produced by it. Rancidity may also be recognised by taste.

2. Heat a portion of the sample in a porcelain or platinum capsule to about 140 or 150°, and observe the odour carefully. When sufficiently cool, pour a little into one hand, rub with the other, and smell again. A little practice will allow of vegetable oils being readily distinguished from animal oils, and the products of fish and marine mammals from those of terrestrial animals. The odour on heating will also frequently permit the recognition of mineral and rosin oils, and, if the remainder of the sample be strongly heated till it ignites and the flame then blown out, the vapours will often have a characteristic odour.

3. Ascertain the sp. gr. of the sample at 15.5°, if fluid at that temperature; but at the b. p. of water (page 48), if solid at the ordinary temperature. This test is valuable, but if the sample be very old, or a mixture of several substances, or if much free acid be present, the indications are less reliable. An unmixed substance may, as a

rule, be placed in one of the groups on pages 86–7, though this classification must only be regarded as giving a rough preliminary indication. Many of the fats and oils might be classified in more than one of the groups. More definite figures are given in the tables on pages 69–73.

Sperm and bottlenose oils are readily distinguished from shale and petroleum products of similar density by the elaidin test, their saponification values and the quantitative results of their saponification. Their estimation, when mixed with hydrocarbon oils, may be effected as described under "Sperm Oil." Oleic acid is distinguished from hydrocarbons by its solubility in an aqueous solution of sodium hydroxide. Mixtures of oleic acid and hydrocarbons may be analysed by titration with standard alkali. If fixed oils are present, the methods given on page 84 should be used.

Differentiation of Animal and Non-drying Vegetable Oils.—The non-drying vegetable oils may be distinguished from the similar oils of animal origin by their taste and odour on heating. Their iodine values and the m. p. of their fatty acids are higher. Many of the vegetable oils show absorption spectra, which is never the case with the animal oils. The phytosteryl acetate test (*q. v.*) and the oleorefractometer reading are also valuable means of differentiation.

The vegetable non-drying oils may be distinguished from each other by various tests. Rape and mustard oils are distinguished from others by relative insolubility in glacial acetic acid by low saponification values, and by yielding small amounts of an insoluble bromide on treatment with bromine. Bone oil usually gives an orange or reddish-yellow elaidin of a pasty consistence, while lard oil and tallow oil yield a firm product of a pale or lemon-yellow colour. The product from neatsfoot oil is variable.

Coconut olein is distinguished from other vegetable oils by its high saponification value, low iodine value, and the very moderate heating produced by sulphuric acid.

Differentiation of Semi-drying and Non-drying Oils.—The semi-drying oils, of which cottonseed and maize oils are typical, have higher iodine values and sp. gr. than the non-drying oils. They may also be distinguished by the large amount of linolic tetrabromide (m. p. 113 to 114°) which they yield on adding bromine to a solution of their insoluble fatty acids in petroleum spirit or carbon tetrachloride. The nature of the product formed in the elaidin test is also instructive.

OILS.

Substance	Sp. gr. at 15° to 16°				
	0.875 to 0.884	0.884 to 0.912	0.912 to 0.920	0.920 to 0.937	0.937 to 0.970
Vegetable oils,	None.	None.	Jamba Apricot kernel Plum kernel Peach kernel Olive Almond Arachis Rape and Colza Mustard Ravison Hazelnut Eruca sativa seed. Non-drying oils.	Beechnut Brazil nut Camelene Caudle nut Madia Maize Nigerseed Pine nut Safflower Cedar nut Soja bean Pumpkin seed Wheat Cotton-seed Sesame Sunflower Poppyseed Hempseed Linseed (raw) Walnut Coconut olein. Curcas. More or less drying oils.	Grapeseed. Tung. Croton. Castor. Boiled linseed. Blown oils.
Terrestrial animal oils,	None.	None.	Neatsfoot. Bone. Lard oil. Tallow Oil.	None.	None.
Marine animal oils,	Sperm. Bottlenose.	None.	Dolphin.	Whale. Porpoise. Seal. Menhaden. Codliver. Shark-liver. Sardine.	None.
Free fatty acids,	None.	Oleic acid.	Linoleic acid.	....	Ricinoleic acid.
Hydrocarbons,	Shale products. Petroleum products.	Shale products. Petroleum products.	Heavy petroleum products.	Heavy mineral oil.	None.

FATS.

Substance	Sp. gr. at 98° to 100°			
	0.750 to 0.800	0.800 to 0.855	0.855 to 0.863	0.863 to 0.890
Vegetable fats,	None.	None.	Palm oil. Cacao butter. Shea butter.	Palmnut oil. Coconut oil. Japan "wax." Myrtle "wax." Cottonseed "stearin." Palmnut "stearin." Bassia tallow. Borneo tallow. Chinese tallow. Goa butter. Laurel oil. Mafura tallow. Nutmeg butter. Piney tallow.
Animal fats,	None.	None.	Tallow. Lard. Suet. Dripping. Bone fat. Margarine.	Butter-fat. Compound lard.

WAXES, ETC.

Substance	Sp. gr. at 98° to 100°			
	0.750 to 0.800	0.800 to 0.855	0.855 to 0.863	0.863 to 0.877
Vegetable and animal waxes,	None.	Spermaceti. Beeswax. Chinese wax. Carnaüba wax. Wool fat.	None.	None.
Free fatty acids,	None.	Stearic acid. Palmitic acid. Oleic acid.	None.	None.
Hydro-carbons,	Paraffine wax. Ozokerite.	Shale and petroleum products.	Vaseline.	....

The hydrocardon oil produced by the distillation of rosin is not included in these tables, as its high sp. gr. (0.970 to 1.000) places it outside any of the classes. The same remark applies to rosin itself, which is of slightly higher sp. gr. than water, and to coal-tar products of high b. p. which might be mistaken for, or found mixed with, the fixed oils.

Differentiation of Drying and Semi-drying Oils.—The drying oils differ from the semi-drying oils in having a higher iodine value, and in yielding a solid film in a short time, when exposed to the air in a thin layer. Some of them give insoluble bromides on treatment with bromine, and an insoluble deposit of linolenic hexabromide (m. p. 180 to 181°) on brominating a solution of their fatty acids.

Differentiation of Drying and Marine Animal Oils.—These oils, which often have similarly high iodine values, are best distinguished by the behaviour of the deposit formed in the *insoluble bromide test* (*q. v.*) when heated, and the nature of the unsaponifiable matter. The sulphuric acid colour test and Livache's drying test will also afford valuable information in the case of mixtures. On saponification, marine animal oils give a much darker soap solution than linseed or other drying oils.

They may be distinguished from one another by their analytical values (see tables). Porpoise oil and some varieties of whale oil contain a notable proportion of esters of lower acids, and give characteristic Reichert-Meissl values.

Differentiation of Various Oils.—Oils of sp. gr. above 0.937 are few and easily distinguished. Croton and castor oil are purgative and readily soluble in alcohol, but have little further resemblance. Boiled linseed oil and Japanese wood (tung) oil have sp. gr. between 0.937 and 0.950, dry rapidly on exposure, and give a firm brown or black clot with sulphuric acid. Blown oils closely resemble castor oil, but may be distinguished as described in the section treating of that oil. Rosin oil has a sp. gr. exceeding 0.970, and is not saponified to any considerable extent by alkalies. It is readily identified by its strong after-taste, and the odour of turpentine developed, when the sample is heated till it catches fire and the flame then blown out. Mixtures of rosin oil with fatty oils may be analysed as described on page 84.

Hydrocarbons and Waxes.—The solid hydrocarbons having a density below 0.800 at the b. p. of water are described under "Paraffine Wax."

The distinctions between the various waxes are fully indicated in the table on page 73, and in the special sections on "Spermaceti," "Beeswax," and "Carnaüba Wax." Free acids are at once distinguished from the waxes by their solubility in alcohol, behaviour with alkalies, and their saponification values; from each other by their

m. p. and combining weights. Vaseline and similar hydrocarbons are sharply distinguished from the waxes and fatty acids by being incapable of saponification.

Differentiation of Animal and Vegetable Fats.—These are best differentiated by the phytosteryl acetate test (*q. v.*), and distinguished from one another by a comparison of the various analytical values.

Coconut and palmnut oils are soft, melt readily, and have high saponification values, fairly high Reichert-Meissl values and low iodine values. Japan and myrtle wax are hard, wax-like bodies of comparatively high m. p. (See "Japan Wax.") Palmnut oil is distinguished from coconut oil and coconut "stearin" by its taste and smell. Butter-fat is the only common fat of animal origin that has a high Reichert-Meissl value.

The nature of the sample having been indicated, further confirmation may be obtained by means of the tables commencing on page 69. The principal fats, oils, and waxes are described at greater length in the following sections.

In the case of a sample consisting of a *mixture of wholly unknown substances*, identification of the constituents is often a difficult problem, but when the leading component is known or can be recognised, the detection of the others becomes more feasible. In most cases oils cannot be recognised by distinct and specific tests, such as exist for the different elements; and, in arriving at a conclusion as to the composition of any sample of mixed oils, the analyst must be content to be guided in a great measure by circumstantial evidence and a careful consideration of probabilities. The foregoing methods of examination are of course employed, and, in addition, such special tests as will be found described under the various heads. The sub-articles descriptive of the more important substances contain a list of the admixtures most commonly found in each and special tests suitable for their detection.

SPECIAL CHARACTERS AND MODES OF EXAMINING FATS, OILS, AND WAXES.

By LEONARD ARCHBUTT, F. I. C.

I. OLIVE OIL GROUP.

Arachis (Earthnut) Oil.
Almond Oil.
Apricot-kernel Oil.
Hazelnut Oil.
Olive Oil.
Olive-kernel Oil.
Peach-kernel Oil.
Plum-kernel Oil.
Tea-seed Oil.

ARACHIS OIL. EARTHNUT OIL. GROUND-NUT OIL. PEANUT OIL.

(See also p. 69.) Earthnut oil is obtained from the nuts of *Arachis hypogæa*, a leguminous creeping plant indigenous to India and the coasts of South Africa and South America, and now cultivated in many countries, the oil being expressed chiefly in France. The seeds contain about 45% of oil, which in India is called *katchung oil*, and is largely used as a substitute for olive oil. Arachis oil is extracted by cold- and hot-pressure, the cold-pressed oil being extensively used as a salad oil and for burning, and the hot-pressed oil for soap-making.

Arachis oil is usually pale greenish-yellow, and of a peculiar nutty flavour and smell, but may be prepared nearly colourless and almost tasteless. It becomes turbid at about 3°, and solidifies at −3° to −4° (Schaedler). The sp. gr. at 15 to 15.5° usually ranges from 0.916 to 0.920, but values ranging from 0.911 (Sadtler) to 0.9256 (Crossley and Le Sueur) have been recorded.

Arachis oil contains olein, hypogæin, linolin, palmitin (?), stearin, arachidin and lignocerin.

Sadtler[1] obtained the following results with arachis oil from various sources.

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[1] *Amer. Jour. Pharm.*, 1897, 69, 490.

	Oil from Virginia nuts	Oil from Spanish nuts	Oil from African nuts	Oil from puducheri	Commercial oil
Sp. gr. at 15°	0.917	0.9175	0.911	0.920	0.9209
Saponification value	192.53	190.68	194.0	193.1	192.1
Iodine value	91.75	94.17	85.6	95.	98.4
Hehner value	94.87	95.31	....	....	95.86
Reichert-Meissl value	0.48	1.60	....	....	....
Free acid as oleic, %	0.55	0.79	0.62	....	6.20
Cold test	+3°	+3°	+2°	....	+10°
Maumené test	56.75°	....	....	49°	45.5°
M. p. of fatty acids	29°	34°	30°	29°	28°
Solidifying point of fatty acids	27.5°	32.5°	29°	25°	25°

Crossley and Le Sueur[1] have recorded the following values given by 4 samples of genuine arachis oil from Madras.

	1.	2.	3.	4.
Sp. gr. at 15.5°	0.9223	0.9223	0.9256	0.9195
Saponification value	190.1	185.6	194.8	192.1
Iodine value	98.47	98.42	92.43	100.82
Hehner value	95.63	......	......	......
Reichert-Meissl value	nil	nil	nil	nil
Free acid as oleic, %	1.45	2.42	8.28	6.80
Butyro-refractometer, 40°	....	57.5	......	......
Optical rotation, 200 mm., 15°	−0°,7′	+0°,24′	±0°	−0°,7′
Efflux time, Redwood, 70° F., (secs.) of 50 c.c.	350.1	347.0	429.3	306.9

It will be seen from the foregoing that arachis oil exhibits a wide range of values. Schnell[2] found several earthnut oils from West Africa with iodine values from 84.4 to 85.7; others, from the East Indies, had values ranging from 89.7 to 95.0. Values as high as 105 (Oliveri) and as low as 83.3 (Tortelli and Ruggeri) have been recorded.

Some oleo-refractometer values of this oil are given on p. 44. The following are some results of examination of the mixed fatty acids:

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[1] *J. Soc. Chem. Ind.*, 1898, **17**, 989.
[2] *Zeit. Nahr. Genussm.*, 1902, **5**, 961.

		Observer
Sp. gr. at 100°/15.5°	0.846–0.8475	Allen.
Sp. gr. at 100°/100°	0.879	Archbutt.
Titer test	28.1–29.2	Lewkowitsch.
Refractive index at 60°	1.4461	Thoerner.
Iodine value of mixed fatty acids	99.5–103.4	Various.
Iodine value of liquid fatty acids	105–129	

Arachis oil contains from 4.3 to 5.4% of arachidic and lignoceric acids, which, owing to their sparing solubility in cold alcohol, can be isolated without much difficulty. Olive and most other oils, except those of rape and mustard seed, contain not more than traces of these acids. Upon this difference in composition, Renard[1] based the following process for the detection and estimation of arachis oil, which is described with some modifications in detail introduced by Archbutt:[2]

10 grm. of the oil are saponified in a deep porcelain basin with 8 c.c. of sodium hydroxide solution (containing approximately 50 grm. sodium hydroxide in 100 c.c.) and 70 c.c. of alcohol, boiled down gently to about 20 c.c., rinsed with hot water into a separating funnel, decomposed with hydrochloric acid in excess, and shaken with ether to extract the fatty acids. After distilling off the ether in an 8-oz. wide-necked flask, the fatty acids are dried by heating the flask on a steam-bath and sucking out the vapour, and are then dissolved by pouring 50 c.c. of rectified alcohol (sp. gr. 0.834) into the hot flask.

To the solution, which should not be hotter than 43°, and must not be allowed to cool below 38°, lest crystals of fatty acids should separate, 5 c.c. of a 20% aqueous solution of lead acetate are added, which will precipitate the whole of the arachidic and lignoceric acids as lead salts, together with some lead stearate and oleate.[3] After cooling to about 15° and allowing to stand for half an hour, the alcoholic liquid is decanted through a filter, and the lead soaps are washed on the filter once with ether. They are then rinsed back into the flask and digested with ether, again filtered and again rinsed back and digested with ether. After doing this about 4 times, using the same filter each time, all the soluble lead salts will have been dissolved out. The extraction with ether should be continued until the washings give no colour, or only a pale brown colour, when shaken with aqueous hydrogen sulphide.

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[1] *Compt. rend.*, 1871, 73, 1330.

[2] *J. Soc. Chem. Ind.*, 1898, 17, 1124.

[3] This quantity of lead is sufficient for 10 grm. of arachis oil. If more is added, a larger precipitate is produced, containing more lead oleate, which takes more washing out with ether, but no more arachidic and lignoceric acids are obtained.

The filter paper containing the lead arachidate, etc., is opened in a large plain funnel placed in the neck of a separating funnel, and, before the soaps have had time to dry, they are rinsed into the separator with a jet of ether from a washing bottle. The soaps which adhere to the paper and flask may be decomposed and transferred by rinsing with warm dilute hydrochloric acid, followed with ether. About 20 c.c. more hydrochloric acid (1.10 sp. gr.) are poured into the separator, which is stoppered and shaken until all the lead salts are decomposed. The aqueous liquid is then run off, and the ethereal solution of the fatty acids washed with small quantities of water until the lead chloride is removed. The ether is distilled off in an 8-oz. flask, and the residual fatty acids are heated in the water-oven until dry. They are then dissolved by warming with 50 c.c. of 90% ethyl alcohol (sp. gr. 0.8340), and the solution is cooled to 15°, when arachidic and lignoceric acids, if present, will crystallise out, either at once or after standing a short time. The flask should be closed by a cork carrying a thermometer.

According to Tortelli and Ruggeri,[1] a rough estimate of the amount of earthnut oil present may be made at this stage by observing the temperature at which the crystals commence to form. For this purpose the liquid in the flask must be heated until the crystals have redissolved, and then allowed to cool slowly.

Temperature at which the crystals commence to form; °	Earthnut oil; %
35–38	100
31–33	60
28–30	50
25–26	40
22–24	30
20.5–21.5	20
18–20	10
16–17	5

In order to estimate the proportion of earthnut oil more accurately, the liquid is allowed to stand from 1 to 3 hours, with occasional agitation, at 15° or 20°, or at some intermediate temperature which is nearest to that of the laboratory; the crystals are then collected on a small filter placed over a 100 c.c. cylinder, using the filtrate alone to rinse out the flask, and are washed several times with small quantities of 90% alcohol until the filtrate and washings measure 70 to 80 c.c., unless the quantity of crystals obtained is very small, in which case less may be used.[1] The filtrate and washings with 90% alcohol must be measured. The crystals are then washed thoroughly with 70% alcohol (sp. gr. 0.8898) in which arachidic and lignoceric acids are quite insoluble. These washings are not measured, but the washing is continued until a few c.c. of the filtrate remain clear when diluted with water in a test-tube, showing that all soluble fatty acids have been washed out. The washed crystals are then dissolved off the filter with boiling ether, distilled down in a tared flask, and dried in the water-oven until constant in weight, for which one hour or less usually suffices. Finally the m. p. is determined by capillary tube, or preferably by Bensemann's method, and the point of incipient fusion should not be lower than 71°.

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[1] *Chem. Zeit.*. 1898, **22**, 600.

Instead of weighing the crystals at this stage, Tortelli and Ruggeri recommend redissolving them in 50 c.c. of 90% alcohol, recrystallising for 1 hour at the same temperature as before, again filtering and washing, first with 90% and then with 70% alcohol, and then weighing. The crystals from pure earthnut oil, when thus purified, melt, by Bensemann's method, at 72.3 to 73.3°.[2] This recrystallisation is essential in the case of some Tunisian olive oils (Archbutt[3]), mixtures containing cottonseed oil (Tortelli and Ruggeri), and solid fats such as lard (Smith[4]), which contain large percentages of saturated fatty acids, and must always be resorted to if the m. p. of the first crop of crystals falls below 70°.

As the mixed acids are slightly soluble in the 90% alcohol used for recrystallisation and washing, a correction must be made, which was given by Renard as 0.0025 grm. for each 10 c.c. of 90% alcohol used in the crystallisation and washing of the acids, if the manipulation was conducted at 15°; or a correction of 0.0045 grm. per 10 c.c., if at a temperature of 20°. But Tortelli and Ruggeri have shown that the correction varies according to the weight of mixed acids obtained. The following table contains their experimental results:

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[1] It is a good plan to do this washing with 3 separate quantities of alcohol, either 10 c.c. or 5 c.c. each, according to the size of the precipitate, and, after collecting the washing each time in a small beaker, to pour it back through the filter 2 or 3 times, so as to saturate it thoroughly before adding it to the main filtrate. Obviously, this must be done at the same constant temperature as that at which the crystallization took place. A paper filter may be used, but a Gooch filter used with moderate suction is better, because the crystals can be more completely separated from the mother liquor.

[2] Tortelli and Ruggeri found the m. p. of the recrystallised acids, determined by capillary tube, between 74° and 75.5°.

[3] *J. Soc. Chem. Ind.*, 1907, **26**, 454 and 1185.

[4] *J. Amer. Chem. Soc.*, 1907, **29**, 1756.

Weight of fatty acids (grm.)	M. p. °	Solubility in 100 c.c. of 90% alcohol at			Obtained from
		15°	17.5°	20°	
2.7000	74.3–74.5	0.0729	0.0820	0.0910	More than 20 grm. arachis oil.
1.5600	75.1–75.5	0.0715	0.0801	0.0922	
1.2506	74.8–75.5	0.0730	0.0811	0.0902	
1.0000	74.3–74.5	0.0688	0.0866	0.0914	About 20 grm. of arachis oil.
0.9604	74.0–74.6	0.0680	0.0869	0.0918	
					20 grm. of a mixture containing
0.5503	74.0–74.6	0.0650	0.0806	0.0879	50% arachis oil.
0.5008	74.0–74.6	0.0643	0.0799	0.0844	
0.3899	74.4–75.5	0.0602	0.0673	0.0740	40%
0.2615	74.0–75.0	0.0539	0.0610	0.0680	27%
0.1690	74.0–75.0	0.0447	0.0544	0.0662	18%
0.1064	74.0–75.0	0.0343	0.0402	0.0472	11%
0.0504	74.4–75.5	0.0301	0.0398	......	5%
0.0505	74.2–74.6	0.0314	0.0410	......	

By plotting these results the following table of corrections has been constructed:

Weight of mixed acids obtained (grm.)	Correction (grm.) to be added per 100 c.c. of 90% alcohol used for crystallisation and washing at		
	15°	17.5°	20°
0.05	+0.031	+0.040	+0.046
0.10	0.036	0.045	0.052
0.20	0.048	0.056	0.062
0.30	0.055	0.064	0.071
0.40	0.061	0.071	0.078
0.50	0.064	0.076	0.084
0.60	0.066	0.080	0.088
0.70	0.067	0.082	0.090
0.80	0.069	0.083	0.092
0.90	0.070	0.084	0.092
1.00	0.071	0.084	0.091
2.70	0.073	0.082	0.091

The percentage of crude arachidic acid isolated from pure earthnut oil by Renard, De Negri and Fabris, Allen, Tortelli and Ruggeri, and Archbutt has varied from 4.28 to 5.50%, averaging about 4.8%. Therefore, the weight of mixed acids obtained, multiplied by 21, is approximately equal to the weight of arachis oil in the quantity of oil taken for experiment.

The degree of accuracy obtainable by this method has been tested by experiments with known mixtures of olive oil and arachis oil. Thus, De Negri and Fabris,[1] working on 10 grm. of oil, obtained the following results:

Arachis oil taken, %...	30	20	15	10	10	10	10
Arachis oil found, %...	29.1	20.2	14.0	10.3	?	9.5	?

Tortelli and Ruggeri, working on 20 grm. of a mixture of olive, sesame, rape, cotton, maize, and arachis oils, and recrystallising the crude arachidic acid, obtained the results set out in the following table:

Compn. of oil tested		Volume of alcohol Temperature Solubility Coefficient	Arachidic and lignoceric acids				M. p. °	% of arachis oil found
Arachis oil	Olive oil		Dissolved in 90% alcohol	Weighed	Total			
					in 20 grm. oil	%		
100		260 c.c. 15° 0.068	0.1768	0.8894	1.0662	5.3300	74.1– 74.3	100
60	40	150 c.c. 17.5° 0.08	0.1200	0.5231	0.6431	3.2155	74– 74.6	60
50	50	250 c.c. 15° 0.06	0.1500	0.3931	0.5431	2.7155	74– 74.6	50
40	60	280 c.c. 15° 0.06	0.1509	0.2770	0.4279	2.1395	74.5– 75.1	40
30	70	260 c.c. 15° 0.05	0.1300	0.2056	0.3356	1.6780	74.1– 74.6	31
20	80	250 c.c. 15° 0.046	0.1150	0.1260	0.2410	1.2050	73.9– 74.4	22
10	90	220 c.c. 15° 0.031	0.0682	0.0514	0.1196	0.5980	72.2– 74.6	11
5	95	150 c.c. 15° 0.03	0.0434	0.0241	0.0675	0.3375	73– 73.5	6.7

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[1] Lewkowitsch, Oils, Fats and Waxes, **2**, 253.

Archbutt, using 10 grm. of oil and following the method already described, obtained the results given below:

Composition of oil taken		Volume of 90% alcohol Temperature Solubility Coefficient	Mixed arachidic and lignoceric acids					Arachis oil found, %
Olive oil	Arachis oil		Dissolved in the alcohol	Weighed	Total	%	M. p. by capillary tube	
	100	80 c.c, 15° 0.063	0.0504	0.4480	0.4984	4.98	71°	
90	10	73 c.c. 15° 0.031	0.0226	0.0265	0.0491	0.491	71°	9.9
80	20	73 c.c. 15° 0.033	0.0241	0.0715	0.0956	0.956	71°	19.2

Instead of isolating the arachidic acid by fractional precipitation of the free fatty acids with lead acetate, as described above, Lewkowitsch[1] prefers to neutralise the soap solution with acetic acid, using phenolphthaleïn as indicator, and to precipitate the whole of the soaps with lead acetate in excess. The lead salts are filtered off and extracted with ether in a Soxhlet apparatus, thus separating the lead salts of the unsaturated fatty acids from the insoluble lead salts of the saturated fatty acids. The latter are then decomposed with hydrochloric acid in the presence of ether, and the ethereal solution having been separated and the ether distilled off, the residual fatty acids are dissolved in alcohol and crystallized as already described.

Tortelli and Ruggeri proceed in a somewhat similar manner. They take 20 grm. of the sample, saponify with alcoholic potassium hydroxide and neutralise with acetic acid. The neutral soap solution is poured gradually into a wide-necked flask containing a boiling-hot solution of 20 grm. of lead acetate in 300 c.c. of water, and the whole is well shaken for 10 minutes in boiling water. The lead salts are thus caused to adhere to the walls of the flask, and the clear liquor having been poured off, the soaps are washed three times with hot water, then cooled, dried with filter-paper, and boiled with 220 c.c. of ether for 20 minutes under a reflux condenser. After cooling the flask in running water for half an hour, the ethereal solution is passed through a filter-paper into a separating funnel, and the residue again boiled with 100 c.c. of ether. This is poured through the filter, and the insoluble soaps are then brought on to the filter and thoroughly washed with ether. The ethereal solution of the lead salts of the unsaturated acids is decomposed with hydrochloric acid, and the fatty acids obtained are used for the silver nitrate test for cottonseed oil and the furfural test for sesame oil, which are said to be absolutely characteristic under these conditions, since neither test is given by the unsaturated fatty acids of any other edible oil. The lead salts of the saturated acids are decomposed with hydrochloric acid in presence of ether, and the crude arachidic acid is isolated in the manner already described.

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[1] Oils, Fats and Waxes, Vol. 2, 252.

F. Jean[1] has proposed a process based upon qualitative tests by Girard and Blarez. 10 grm. of the oil are saponified by being heated at 110° with a mixture consisting of 3 grm. of potassium hydroxide dissolved in 3 or 4 c.c. of water and 5 c.c. of alcohol at 36°. The mass is well stirred with a spatula, the heating continued till the soap becomes dry, when it is transferred to a flask and mixed with 100 c.c. of alcohol at 36°, previously saturated with potassium arachidate at 11° to 12°. The flask is warmed under a reflux condenser until the soap dissolves, and is then left for 12 hours at a temperature of 15°. The precipitate is filtered off and re-crystallised in the same way from the saturated alcohol. It is then collected, transferred to a flask, and boiled with 50 c.c. of water containing some hydrochloric acid, in order to liberate the arachidic acid. The latter is subsequently extracted with petroleum ether in a separating funnel, and after evaporation of the solvent dried at 100° and weighed. Its m. p. should not be lower than 72°.

J. Bellier[2] has proposed the following simple qualitative test for arachis oil in olive oil, which the reviser can recommend from personal experience. Solutions required are:

Alcoholic potassium hydroxide, made by dissolving 8.5 grm. pure potassium hydroxide in 70% alcohol and making up to 100 c.c.

Acetic acid of such strength that 1.5 c.c. will exactly neutralise 5 c.c. of the alkali solution [120 c.c. of British Pharmacopœia (36%) acetic acid diluted with water to 150 c.c. is, approximately, of the right strength].

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[1] *Rev. de Chim. Ind.*, 1898, **9**, 162.
[2] *Ann. de Chim. Anal.*, 1899, **4**, 4.

Weigh 1 grm. of the sample into a dry boiling tube, add 5 c.c. of the alkali solution and boil gently over a small flame, holding the tube in the hand, until saponification is complete, which will take rather more than 2 minutes, avoiding evaporation as far as possible. Add 1.5 c.c. of the acetic acid, or just sufficient to neutralise the 5 c.c. of alkali solution, mix well, rapidly cool by placing in water at 17° to 19° and leave in the water for about 30 minutes (*not less*), shaking occasionally. Then add 50 c.c. 70% alcohol containing 1% by volume of hydrochloric acid (1.16), shake well, and again place in the water for 1 hour. If no arachis oil be present, a clear or opalescent liquid is formed; if more than 10% of arachis oil be present, a flocculent, crystalline precipitate remains; even with 5% of arachis oil a distinct precipitate remains and separates on standing.

Industrial neutral olive oils, known in commerce as "Saponified Oils" and prepared from the olive residuum oils and oils of the third pressing, which frequently contain as much as 3% or even more of unsaponifiable matter, apparently derived from the shell of the olive kernel, may give a flocculent precipitate in Bellier's test, though free from arachis oil.

For the *quantitative* estimation of arachis oil, Bellier takes 5 grm., saponifies with 25 c.c. of the alcoholic alkali solution, exactly neutralises with acetic acid, and places in running water for 1 hour. The precipitate is collected on a filter, and washed with 70% alcohol containing 1% of hydrochloric acid (1.16) at 15°–20°, until the filtrate does not become perceptibly turbid on the addition of water. The residue is dissolved off the filter with 25 to 50 c.c. of boiling rectified alcohol, which is then mixed with sufficient water to reduce the strength to 70%, and kept at 20° for 1 hour. The crude arachidic acid is filtered, washed with 70% alcohol free from hydrochloric acid, and weighed. The m. p. should be about 72°. By this process, Bellier obtained 4.2% of crude arachidic acid from Bordeaux earthnut oil and 4.17% from a sample of Marseilles oil. A large number of European and African olive oils which were examined yielded from nil to 0.060% of fatty acid, the latter amount, corresponding to 1.44% of earthnut oil, being obtained from an oil from Tunis. Known mixtures of olive oil and arachis oil gave correct results when analysed by this process. Samples of cottonseed oil and sesame oil also gave small quantities of insoluble acids corresponding to 0.72 and 0.48%, respectively, of earthnut oil. This process is much shorter than Renard's, but needs further investigation. The reviser has obtained good results by the qualitative, but low results by the quantitative method.

In the examination of samples of arachis oil for adulterants, an estimation of the crude arachidic acid should be made, as it is the most characteristic test for this oil. Tortelli and Ruggeri found the following percentages in arachis oil from different sources:

Description of arachis oil	Crude arachidic acid; %	M. p.; °
Buenos Ayres, expressed at 45° to 50°	5.24	74.4–74.7
Buenos Ayres, extracted with ether	4.92	74.2–74.8
Ruffisque, extra, 1st pressing	4.31	74.2–74.6
Ruffisque, fine, 2d pressing	4.55	74.4–75.2
Gambia, extra, 1st pressing	4.59	74.5–75.1
French (commercial oil)	5.33	74.1–74.4
Spanish (commercial oil)	5.40	74.3–75.4

Sesame oil should always be looked for, as it is frequently present in large quantity. Soltsein[1] found it by the Baudouin test in all samples of commercial arachis oil examined by him, and states that it is customary to add sesame oil to the finest grades of arachis oil with the object of lowering the cold test and improving the miscibility of the oil for salads. As arachis oil is frequently offered as a lubricating oil in place of olive oil, the absence of sesame oil is important, as even genuine arachis oil has more strongly marked drying properties than olive oil, and any addition of sesame oil increases the tendency to oxidise. Sesame oil may be detected by the furfural test. It will raise the sp. gr., also the iodine, Maumené, and oleo-refractometer values. Sesame oil contains more linolic acid than arachis oil.

Poppy oil would also raise the sp. gr., iodine value, Maumené value and oleo-refractometer value of arachis oil, and would lower the solidifying point of the oil and of its mixed fatty acids, as well as increasing in a marked degree the tendency to oxidise.

Cottonseed oil would be indicated by Halphen's colour test, and by the much higher iodine value of its liquid fatty acids and much larger yield of tetrabromides.

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[1] *Chem. Rev. Fett-Harz-Ind.*, 1901, **8**, 202.

Rape oil would lower the saponification value and increase the viscosity in a marked degree.

ALMOND OIL.

(See also p. 69.) Almond oil is a fixed oil expressed from either sweet or bitter almonds, the kernels of *Prunus amygdalus*. The oil of commerce is mostly obtained from bitter almonds (*P. amygdalus amara*), the marc of which is then distilled with water to obtain the essential oil. Fixed oil of almonds must not be confounded with the essential oil of bitter almonds. It is largely employed in the preparation of ointments and emulsions, for which it is better adapted than olive oil.

Almond oil is nearly odourless, of a straw-yellow colour and bland taste. It does not solidify till cooled to about −20°, some samples only becoming turbid at that temperature. According to the German Pharmacopœia, almond oil should remain clear when exposed to a temperature of −10°. The sp. gr. ranges from 0.914 to 0.920.[1] It is soluble in 24 parts of cold alcohol or in 6 parts at the b. p. It consists chiefly of olein and a small quantity of linolin.[2] Only small quantities of solid glycerides are present, and no stearin.[3] It is not a drying oil and, according to Lewkowitsch, does not easily turn rancid.

The chief physical and chemical constants of this oil are given on p. 69 and the oleo-refractometer value on p. 44. 7 samples of oil from sweet and bitter almonds tested by Lewkowitsch[4] in the butyro-refractometer at 40° gave numbers ranging from 56.5 to 57.5. The refractive indices of 35 samples determined by Harvey[5] in the Abbe refractometer ranged from 1.4702 to 1.4709 at 20°.

The mixed fatty acids have an exceptionally low m. p. (see p. 69). According to the German Pharmacopœia, they should remain permanently fluid at 15°, should give a clear solution with an equal volume of alcohol at 15°, and this solution should remain clear on adding twice the volume of alcohol.

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[1] Most observers give a smaller range (0.9175 to 0.920 at 15.5°).
[2] Farnsteiner. *Zeit. Nahr. Genussm.*, 1899, **2**, 1.
[3] Hehner and Mitchell. *Analyst*,, 1896 **21**, 316.
[4] *Analyst*, 1904, **29**, 105.
[5] *J. Soc. Chem. Ind.*, 1905, **24**, 717.

The following are some further results of the examination of the mixed fatty acids of almond oil:

	Sweet almonds	Bitter almonds	Observer
Solidifying-point (titer test)	9.5–10.1	11.3–11.8	Lewkowitsch
Refractive index	1.4461	1.4461	Thoerner
Iodine value of mixed fatty acids.	93.5–95.5	94.1–96.5	De Negris and Fabris
Iodine value of liquid fatty acids.	101.7	......	Tortelli and Ruggeri

Commercial Almond Oil.—Almond oil is frequently adulterated with, and sometimes entirely substituted by peach-kernel or apricot-kernel oil, which is sold in England as "foreign almond oil," or "oil of sweet almonds, French" (*oleum amygdalarum gallicum*). Genuine almond oil is sold under the name of "Almond oil, English." Olive, lard, arachis, rape, sesame, cottonseed, and poppy oils are also liable to be employed as adulterants.

Many of these additions may be detected by observing the absorption spectrum of the sample, almond oil differing from most vegetable oils in not giving either a banded spectrum or producing strong absorption in the red or violet.

Lard oil and olive oil are indicated by the formation of a white granular deposit when the sample is exposed to a temperature of —5° for 20 minutes, by the high m. p. of the mixed fatty acids and by their incomplete solubility in alcohol at 15°. Lard oil will be further indicated by the odour developed on warming the sample, and especially by the phytosterol acetate test (see under "Cholesterol").

Arachis oil may be detected by Renard's test (see "Arachis Oil"); *rape oil* by the reduced sp. gr. and saponification value of the sample; *cottonseed oil* by Halphen's colour test, as well as by the high m. p. of its mixed fatty acids and its marked drying properties; *sesame oil* by the Baudouin colour test; and *poppyseed oil* by the increased iodine value, refractive power, and Maumené thermal value of the sample.

The detection of the last-mentioned oils presents no great difficulty. It is otherwise with *apricot-kernel* and *peach-kernel* oils, which so closely resemble almond oil that the ordinary tests are not available. Apricot-kernel oil has a somewhat higher average iodine value than almond oil, but the difference is not great enough and the results given by almond oils from different sources are too variable, for any definite conclusion to be based upon this test in the case of mixtures. Further investigation of the liquid fatty acids might lead to a test based upon a difference in the yield of tetrabromides, as Lewkowitsch[1] has suggested, and an observation by Dieterich[2] that the critical temperature of solution determined by Crismer's method (p. 63) of almond oil is much lower than that of apricot-kernel oil or peach-kernel oil is also worth following up. In the present state of our knowledge, recourse must be had to colour tests, of which the following are available:

Bieber's Test.—5 volumes of the sample are shaken with 1 volume of a cold mixture of strong sulphuric acid, water, and fuming nitric acid in equal parts by weight. Pure almond oil gives a white or yellowish-white liniment, apricot-kernel oil a deep salmon-red or peach-blossom colour, changing to dark orange. Lewkowitsch recommends this test in preference to others. The reagent should be freshly prepared. Mixtures of almond oil and apricot-kernel oil containing 1/3 of the latter are distinctly coloured, but with 25% the colour is slight. Peach-kernel oil gives the same test much more faintly and only after standing for some time; this oil will, therefore, be still more difficult to detect in mixtures.

Kreis' Phloroglucinol Test.[3]—A few c.c. of the sample of oil are poured upon an equal volume at nitric acid of 1.4 sp. gr.; a similar quantity of a 0.1% solution of phloroglucinol in ether is then added and the whole well shaken together. Peach-kernel and apricot-kernel oils give an intense raspberry-red colour, inclining to violet. Chwolles, who recommended this test, found that genuine almond oil gave no colour or only a faint rose-red colouration and that 10% of peach-kernel oil could be detected in admixture, but Lewkowitsch found that several genuine almond oils gave the coloration more or less strongly and recommends great caution in the use of this test. It should be noted that the raspberry-red colour is also obtained with arachis, sesame, cottonseed, walnut, and castor oils, but not with olive or lard oils (Kreis).

Nitric Acid Test.—Almond oil, if shaken with nitric acid of 1.4 sp. gr. becomes pale yellow; apricot-kernel and peach-kernel oils become orange-coloured (Micko). According to the British Pharmacopœia, if 2 c.c. of almond oil "be well shaken with 1 c.c. of fuming nitric acid and 1 c.c. of water, a whitish, not brownish-red, mixture should be formed, which, after standing for 6 hours at about 10°, should separate into a solid white mass and a nearly colourless liquid (absence of peach-kernel and other fixed oils)." The United States Pharmacopœia and the Swiss Pharmacopœia also give this test for the detection of peach-kernel oil, but Umney[1] found the test incapable of detecting peach-kernel oil, though useful for detecting apricot-kernel oil. F. B. Power, in a paper read before the British Pharmaceutical Conference in July, 1900, suggests as an explanation of this apparent discrepancy the statement of Hirsch that "Pfirschkernöl," for which the Swiss Pharmacopœia gives the test with fuming nitric acid as specific, is not the oil from the kernels of the common peach, but from a small sort of the bitter almond, *Amydgalus communis.* This oil, Power states, shows the behaviour described in the Pharmacopœia.

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[1] *Analyst*, 1904, **29**, 107.
[2] See Wright and Mitchell, Oils, Fats, Waxes, etc., p. 403.
[3] *Chem. Zeit.*, 1902, **26**, 897.

APRICOT-KERNEL OIL.[2] PEACH-KERNEL OIL.[2] PLUM-KERNEL OIL.

(See also p. 69.) These three oils, obtained, respectively, from the kernels of the apricot, *Prunus armeniaca*, the peach, *Amygdalus persica*, and the plum, *Prunus domestica*, closely resemble almond oil, for which they are largely used as adulterants and substitutes (see "Almond Oil"). Apricot and peach-kernel oils are known commercially as *Ol-Amygdalæ Persic.* (Squire).

HAZELNUT OIL.

(See also p. 69.) This is a golden-yellow coloured, non-drying oil, obtained from the seeds or nuts of *Corylus avellana*, the common hazel. The nuts contain from 50 to 60% of the oil. It is used in perfumery, in pharmacy, and also as a lubricant for clocks.

Hanus[3] states the composition of the fatty acids of this oil to be, oleic acid 85, palmitic and stearic acids 10. About 1% of stearic acid was found, but no arachidic acid, and no linolic or linolenic acid. The oil forms a green-coloured, solid elaidin. It contains about 0.5% of phytosterol. Hanus obtained the following values:

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[1] *Pharm. Jour.* July, 1899, p. 106, and Jan., 1900, p. 8.

[2] See Lewkowitsch, *Analyst*, 1904, **29**, 105.

[3] *Zeit. Nahr. Genussm.*, 1899, **2**, 617.

	Oil	Mixed fatty acids	Liquid fatty acids
Sp. gr. at 15°	0.9169		
Maumené test	36.2°		
Saponification value	193.7	200.6	198.5
Iodine value	90.2	90.6	91.3
Hehner value	95.6		
Reichert-Meissl value	0.99		
Acetyl value	3.2		

Tortelli and Ruggeri found the iodine value of the cold-pressed oil to be 83.9, and that of the liquid fatty acids 97.6, which points to the presence of fatty acid more unsaturated than oleic.

OLIVE OIL.

(See also p. 69.) Olive oil is expressed from the fruit of the olive, *Olea europæa*, and oil of inferior quality is extracted from the residual marc by carbon disulphide ("sulphocarbon oil") or petroleum ether. Peano[1] states that in determining the oil in olives, carbon disulphide should be used and not ordinary ether, as the latter dissolves another substance.

Of the commercial varieties, Provence and Tuscan oils are among the most esteemed. The finest grade in the market is "finest cream sublime oil," which is imported from Leghorn. Oils of other origin are Gallipoli, Sicilian, Spanish, Portuguese, Levant, and Mogador. That sold in the so-called "Florence flasks," is usually of inferior quality. Lucca and Gallipoli oils are well-known brands, and much excellent oil is expressed in Spain, and exported from Malaga and Seville. Olive oil is now largely prepared in California, Tunis, Algeria, and Morocco. Much African oil goes to Nice and is there blended with the oil of the district and sold as pure Nice olive oil.[2]

The oil which exudes from the ripe olives under moderate pressure in the cold is sold as "virgin," "sublime," or "first expressed" oil; it is the best edible oil. Ordinary oil, from a second pressing with the aid of hot water, has a less agreeable flavour than the first and is more liable to become acid, but the two sorts are often mixed, forming several varieties. "Pyrene'" oil, "bagasses" oil, "huile tournante," "huile d'enfer," etc., are very impure acid oils, recovered from residues which have fermented. Industrial neutral olive oils, known as "saponified" oils, are prepared from these residuum oils and oils of the third pressing by washing with alkali to remove the free fatty acid.

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[1] *J. Soc. Chem. Ind.*, 1903, **22**, 35.
[2] *Chemist and Druggist*, Aug. 19, 1905.

The variations in the quality are largely dependent on the manner in which the olives are treated, as, *e. g.*, the care with which the fruit is plucked, the length of time it is stored before being crushed, etc. The flavour of the oil, which largely governs its commercial value for edible uses, apart altogether from its purity or genuineness, depends upon the variety of olive from which the oil is expressed, the degree of ripeness of the fruit when picked, and the process of extraction.

In some countries olive oil is an important article of diet. It is employed in the manufacture of woollen cloth, and in dyeing fabrics turkey-red, though its application for these purposes is decreasing. The inferior varieties are employed in soap making. It is highly esteemed as a lubricant, and is largely employed when price permits. The quantity used in this way depends much on the price of rape oil, which is usually much cheaper, and, though more liable to "gum" than olive oil, is less apt than the latter to become acid.

Olive oil differs in physical characters according to its quality. The finest kinds have a pale yellow colour, with a tinge of green, are almost wholly free from odour, and possess a mild and agreeable taste. Inferior qualities have a greenish-yellow or brownish-yellow colour, an unpleasant odour, and a decidedly acrid after-taste.

The absorption spectrum of the fresh oil shows well-defined chlorophyll bands, which become changed or altogether destroyed on exposure to sunlight or heating with caustic alkali.

When cooled to about 2°, it commences to deposit a white granular fat. At 0° to $-6°$ it solidifies to a product which can be separated by pressure into a solid tallow-like fat and a fluid "oleine."

Chemically, olive oil is chiefly composed of the glyceryl esters of oleic and palmitic acids, with some linolic acid. The proportion of esters of solid fatty acids is very variable in the oils from different sources, and exceptionally large in the Tunisian oils from Sfax and Sousse which, in consequence of their depositing solid fat at temperatures as high as 10°, are "demargarinated" before being placed on the market.[1] The fatty acids exist partly as mixed glycerides. Holde and Stange have isolated about 1.5% of oleo-dimargarin, and Holde has obtained evidence that the remainder of the solid acids are present as mixed esters containing 1 molecule of saturated fatty acid and 2 molecules of oleic acid.[1] Hehner and Mitchell found no stearic acid in olive oil. Minute traces of arachidic acid have been isolated, but not sufficient even in Tunisian oils to lead to erroneous conclusions being drawn from the results of Renard's and Bellier's tests for arachis oil.[2]

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[1] Lewkowitsch. Oils, Fats and Waxes, II, 287.

Olive oil is the type of a non-drying vegetable oil. It does not thicken materially, even on prolonged exposure to air, but gradually becomes rancid, a change which appears to be mainly due to oxidation.[3] In very thin films it dries slowly. The following results obtained by Archbutt [4] show how it compares with some other well-known oils in this respect:

Kind of oil	Time required for a thin film to dry in air at 50° (0.1 grm. oil on a glass surface 7 cm. square)
Olive oil	More than 13 days.
Rape oil	About 48 hours.
Curcas oil	About 24–30 hours.
Cottonseed oil	About 21 hours.
Maize oil	About 18 hours.
Linseed oil	About 12 hours.

If free from acid it is only slightly soluble in alcohol, but dissolves in about 1.5 times its weight of ether, and is miscible in all proportions with carbon disulphide, chloroform, and hydrocarbons.

When heated to about 120°, olive oil becomes lighter in colour, and at 220° nearly colourless and at the same time rancid. At 315° it suffers decomposition, emitting a disagreeable odour of acrolein.

The following are some observed analytical data of the mixed fatty acids of olive oil not given on p. 69:

		Authority
Sp. gr. at 99°/15.5°	0.843	Allen.
Sp. gr. at 100°/100°	0.874–0.876	Archbutt.
Solidifying-point (titer test)	16.9°–26.4°	Lewkowitsch.
Refractive index at 60°	1.4410	Thoerner.
Iodine value of mixed fatty acids	86–90	Various.
Iodine value of liquid fatty acids	92.8–104.2	

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[1] *Ber.*, 1901, **34**, 2402; 1902, **35**, 4036; 1905, **38**, 1247.
[2] Archbutt, *J. Soc. Chem. Ind.*, 1907, **26**, 453 and 1185.
[3] Ryan and Marshall. *Amer. Jour. Pharm.*, 1907, **79**, 308.
[4] *J. Soc. Chem. Ind.*, 1899, **18**, 346.

Assay of Genuine Olive Oil.—Genuine olive oil often contains a notable quantity of free acid, the proportion of which increases by keeping and exposure. In 151 samples from various sources Archbutt found the following percentages of free (oleic) acid:[1]

Number of samples	Source	Free (oleic) acid %		
		Highest	Lowest	Average
70	Spain	25.1	1.5	5.5
36	Italy	25.2	0.9	8.5
28	Sicily	16.6	0.5	9.1
12	Candia	16.8	5.5	9.5
3	Levant	13.5	8.5	10.4
2	Zante	8.7	4.8	6.7

Thomson and Ballantyne[2] and Thomson and Dunlop[3] found in 20 samples of commercial oils from very varied sources free (oleic) acid ranging from 3.86% in a sample from the Levant to 24.72% in a sample of Mogador oil.

Tolman and Munson found in 18 Italian oils from 0.57 to 2.79% and in 38 Californian oils from 0.20 to 3.51%.[4]

The following results were observed by N. J. Lane in the United States Customs Laboratory at New York:[5]

Free fatty acid, %	Number of samples		
	French oil	Italian oil	Total
Not exceeding 3	28	35	63
3 to 5	7	8	15
5 to 10	10	5	15
10 to 20	3	8	11
29.2	1	0	1
	49	56	105

Most of this free acid is caused by allowing the fruit or the pulp to ferment before the oil is expressed from it, or by storing the oil in a crude state.

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[1] *J. Soc. Chem. Ind.*, 1889, **8**, 685.
[2] *Jour. Soc. Chem. Ind.*, 1891, **10**, 233.
[3] *Analyst*, 1906, **31**, 281.
[4] *Jour. Amer. Chem. Soc.*, 1903, **25**, 954.
[5] *Jour. Soc. Chem. Ind.*, 1900, **19**, 223.

It has been shown[1] that if the oil be filtered immediately after expression, to remove the insoluble impurities, the acidity does not increase by storage, or at any rate only very slowly.

Oil intended for table use, for lubricating, and for burning in lamps, should be as free as possible from acid, a maximum of 4% being the desirable limit. In lubricating oils, the free acid corrodes the bearings, forming metallic soaps which dissolve in and thicken the lubricant.[2] In lamp oils excess of acid causes charring of the wick. For soap-making, free acid is no detriment, and for Turkey-red dyeing a very acid oil ("tournante oil") is preferred, as it readily emulsifies with a solution of sodium carbonate. Lewkowitsch states that 25% of free fatty acids should be present in Turkey-red oil. For woolcombers' use free acid is not necessarily objectionable, providing the oil does not form sticky and varnish-like films on the wool. (See below.)

The proportion of free acid in olive oil can be ascertained with ease and accuracy by titration in presence of alcohol with standard caustic alkali and phenolphthaleïn, in the manner described on p. 9.

Burstyn (*Dingl. polyt. J.*, 1875, **217,** 314; *J. Chem. Soc.*, 1876, **29,** 769) has described the following method for estimating the free acid in olive oil. The process appears well suited for rapid technical investigations, though the volumetric method described elsewhere will be preferred by chemists. The oil is shaken with an equal measure of rectified spirit of 0.830 to 0.840 sp. gr., the exact figure being accurately determined. After the liquids have separated, the sp. gr. of the spirit is determined. Burstyn finds that an oil, 100 c.c. of which contains free acid in quantity sufficient to neutralise 1 c.c. of normal alkali (=0.282% of oleic acid), will raise the gravity of the alcohol from 0.830 to 0.8325, and that each additional 1 c.c. of alkali neutralised corresponds to an increase of 0.0003 in the sp. gr. of the spirit. Hence, the increase due to the solution of a trace of neutral fat is 0.0022, and that each increase of 0.0001 in sp. gr. beyond this number represents $\frac{0.282}{3} = 0.094$ grm. of free acid per 100 c.c. Burstyn states that the action of olive oil on brass is regularly and directly proportional to the percentage of free acid present.

In examining oil intended for cooking or table use, the flavour and odour should be carefully observed, as many apparently genuine specimens which are fairly free from acid are unsatisfactory in this respect.

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[1] Milliau, Bertainchaud and Malet. *Monit. Scient.*, 1900, **56,** 508.
[2] Archbutt and Deeley, Lubrication and Lubricants, p. 213.

Richardson and Jaffé[1] find that some olive oils thicken and gum by oxidation much more readily than others, and are, therefore, less suitable for oiling wool. This property has no necessary relation to the percentage of free oleic acid present, but the source of the oil is of far greater importance.[2] In order to test the oxidisability of an oil, they place 10 grm. in a tin tray measuring 4 in. by 6.5 in. by 0.5 in. deep, contained in a special oven,[3] pass over the oil a current of air at 100° for 6 hours or 204° (400° F.) for 4 hours, and determine the time of efflux at 100° of 5 c.c., before and after oxidation, from a jacketted 5 c.c. pipette. The following results were obtained:

Description of oil	Free (oleic) acid, %	Percentage increase of viscosity after heating for	
		6 hrs. at 100°	4 hrs. at 204°
Gallipoli	21.3	10.5	
Seville	3.82	32.6	
Gallipoli	4.23		73
Seville	4.23		644
Levant	12.69		315

These results explain the preference given to Gallipoli oil by wool-combers, but the excessive acidity would be objectionable for lubricating.

EXAMINATION OF OLIVE OIL FOR ADULTERANTS.

Olive oil is very liable to adulteration, the sample being sometimes coloured to give it the appearance of green olive oil. A colouration due to copper can be detected by adding ether and shaking with dilute sulphuric acid, which removes the green colour. On drawing off the acid liquid, copper will be found in it by the usual tests and may be quantitatively determined.

Cottonseed oil is probably the most frequent adulterant of olive oil, especially in America; but arachis, sesame, poppy, lard, and rape oil are also used. Poppy oil, on account of its sweet taste and slight odour, is said to be a frequent adulterant in Europe, but it is doubtful if it is ever used in America (Tolman and Munson). The acrid taste of even refined rape oil would be against its use in edible olive oil, but it might be added to lubricating oil. Maize oil, which is largely produced in America, is a not unlikely adulterant, and has been sold as a substitute for olive oil (see below). Lard oil, expressed at a low temperature and specially refined, is largely used when the price permits of it, "Superfine Lucca oil" being stated to contain sometimes as much as 60 to 70% of it. Fish oils are occasionally employed, menhaden oil being said to be used frequently. Hydrocarbon oils are also used.

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[1] *J. Soc. Chem. Ind.*, 1905, **24**, 534.
[2] See also Milliau, Bertainchaud and Malet, *Monit. Scient.*, 1900, **56**, 508.
[3] Obtainable from Messrs. Reynolds and Branson, Leeds, England.

In the United States, cottonseed oil is largely sold under the name of olive oil. In fact, until the adoption of the recent food laws, especially the Federal act, the label "Huile d'Olive vierge, E. Loubon, Nice," was generally understood in the grocery trade to indicate cottonseed oil. Bulletin No. 77 (1905) of the United States Department of Agriculture contains illustrations of several spurious labels. A bottle labelled "Freres & du Peaux, Bordeaux, France. Huile D Olive" contained cottonseed oil. Another containing mixed olive and cottonseed oil bore the label "Tisserand & Fils. Huile d'Olive extra surfine, Bordeaux, France. Falcon brand." A mixture of olive and peanut oil was described as "Huile D'Olive, extra surfine, Jules Chambon & Cie., Bordeaux, France." This label also bore the signature of the alleged importer. On enquiry at Bordeaux, no trace could be found of the above-named firms, and most likely the labels as well as the oil were of American manufacture. A label of another kind was found on a bottle of maize oil. This, at first glance, appears to read "Superior Olive Oil. Dove Pure Oil Co.," but, on closer inspection, it is seen to bear the words "Superior in quality, purity and flavour to any olive oil in the market."

In examining olive oil, the most important indications are sp. gr., iodine value, saponification value, rise of temperature on treatment with sulphuric acid or bromine, amount and nature of the unsaponifiable matter, some form of oxidation test, and some colour indications. Some sophistications require the application of special methods for their detection.

The *sp. gr.* of olive oil usually ranges from 0.915 (rarely 0.914) to 0.917 at 15.5°, but genuine Tunisian and Californian and even some Italian oils may have as high a sp. gr. as 0.918. Even 0.919 has been recorded for Tunisian oil and 0.9203 for an olive oil from the Punjab.[1] On the other hand, a sp. gr. as low as 0.9122 has been observed in an oil containing 31% of free (oleic) acid.[2] High gravity oils are usually dark in colour, and may contain oil from the kernel and endocarp. All samples over 0.917 in sp. gr. should be submitted to a very critical examination for adulterants. An admixture of rape, lard, or arachis oil would not be indicated by the sp. gr. Cottonseed, poppyseed, or sesame oil would tend to raise it, but the sp. gr. could be adjusted by a judicious mixture of these with sperm or mineral oil which would, however, be readily detected by other tests.

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[1] Crossley and Le Sueur, *J. Soc. Chem. Ind.*, 1898, **17**, 998.

[2] *Bull. No.* 77 (1905) U. S. Dept. of Agriculture, p. 15.

The *iodine value* is a most useful test, but for its correct interpretation a knowledge of the source of the oil is needed. Genuine samples usually absorb from 82.0 to 86.0% of iodine, but lower and higher values may be met with and the oil still be genuine. The results of numerous observers for oils from various countries tabulated by Lewkowitsch[1] range from 77.28 to 94.7. Italian and Spanish oils rarely absorb more than 86% of iodine; the highest iodine values are to be looked for in the oils from California, Tunis, Algiers, Morocco, and Dalmatia. The following values have been recorded for single samples:

Observer	Source of oil	Iodine value
Colby[2]	California	93.5
Crossley and Le Sueur[3]	Punjab	93.67
Ahrens and Hett[4]	Morocco black olives, hand pressed	91.5
Guozdenovic[5]	Dalmatia	92.8
Thomson and Dunlop[6]	Mogador	94.3
Archbutt[7]	Mornag (Tunis). Olive (var.) Chetui.	94.7
	Bizerte (Tunis). Olive (var.) Chetui.	91.1
	Medjez-Amar (Algeria)	90.5

A few varieties of olives grown in certain districts appear to give these exceptionally high results, oils from other varieties and districts giving normal or more nearly normal figures. In ordinary cases, an iodine value of over 87 would indicate adulteration. Goldberg's observation that the solid and liquid portions of chilled olive oil absorb practically the same amount of iodine shows that the iodine value of demargarinated oil is not likely to be appreciably higher than that of the entire oil from the fruit.

[1] Chem. Tech., **2**, 275.
[2] *California Agr. Expt. Sta. Rept.*, 1897–8, 168.
[3] *J. Soc. Chem. Ind.*, 1898, **17**, 989.
[4] *Zeits. Oeffentl. Chem.*, 1903, **9**, 284.
[5] Lewkowitsch, *Chem. Tech.*, **2**, 275 (footnote).
[6] *Analyst*, 1906, **31**, 281.
[7] *J. Soc. Chem. Ind.*, 1907, **26**, 453 and 1185.

Tolman and Munson[1] give a large number of analyses of genuine Californian olive oils obtained from all parts of the State and representing the different soils and climatic conditions. The iodine values of 42 samples ranged from 78.5 to 89.8, with an average of 85.1. 11 samples examined by Blasdale ranged from 80.0 to 86.5; average 84.0. Samples of known purity examined by Colby ranged from 77.7 to 93.5. Tolman and Munson have found that the iodine value increases as the percentage of solid fatty acids and the m. p. of the mixed fatty acids decrease, and they recommend that the iodine value should be considered in conjunction with these other factors and with the iodine value of the liquid fatty acids. They give the following table:

RELATION BETWEEN IODINE VALUE, SOLID FATTY ACIDS AND M. P. OF MIXED FATTY ACIDS (CALIFORNIA OILS).

Iodine value	Solid fatty acids, %	M. p. of mixed fatty acids,°	Iodine value	Solid fatty acids, %	M. p. of mixed fatty acids,°
79.9	10.91	31.0	85.6	4.92	21.3
83.0	7.62	28.0	85.7	6.27	23.4
82.9	5.70	25.0	86.2	3.39	21.1
84.3	7.23	23.4	88.2	4.42	23.5
85.6	5.12	22.6	88.5	2.43	20.2

The same relation was found to hold good in a general way for Italian oils, but Milliau did not find this relation in the oils from Tunis. He found oils, for example, with an iodine value of 88 and a m. p. of fatty acids of 37°. The following table shows the relation between the iodine value of certain olive oils and that of their liquid fatty acids:

Kind of olive oil		Iodine values				
		Of oil		Of liquid fatty acids		
		Tolman and Munson	Tortelli and Ruggeri	Tolman and Munson		Tortelli and Ruggeri
				Determined	Calculated[2]	
Italian..........	Maximum	86.1	85.4	98.4	104.1	101.5
	Minimum	79.2	80.0	89.8	89.1	95.5
	Average	81.6	83.6	94.0	96.5	97.5
Spanish........	Maximum	....	87.2	....	....	104.2
	Minimum	....	78.5	....	....	95.5
	Average	....	85.5	....	....	100.4
Californian.....	Maximum	89.8	....	96.6	98.8	
	Minimum	78.5	....	88.9	90.5	
	Average	85.3	....	92.8	95.0	

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[1] *Bull. No.* 77. U. S. Dept. of Agriculture.

[2] Calculated from the iodine value of the oil, the percentage of solid fatty acids, and the average Hehner value (95.5).

Tolman and Munson have ascertained the iodine values and the solid fatty acids of a number of oils, and they point out that the relation between these numbers gives a great deal more information in the analyses of mixtures than the simple iodine values of the oils themselves. Their results are summarized in the following table.

AVERAGE IODINE VALUES AND PERCENTAGE OF SOLID FATTY ACIDS OF VARIOUS OILS, OBTAINED BY TOLMAN AND MUNSON.

Number of samples	Kind of oil	Iodine value of		Solid fatty acids, %	
		Oil	Liquid fatty acids		
18	Olive (Italian)	81.6	96.5	10.50	Maximum 17.7 Minimum 5.0
39	Olive (Californian)	85.3	95.0	5.86	Maximum 13.0 Minimum 2.0
4	Lard	73.8	99.9	21.58	Maximum 26.7 Minimum 18.9
6	Cottonseed	106.6	138.9	21.17	Maximum 23.6 Minimum 17.9
4	Rape	96.9	102.1	0.64	
3	Mustard	107.3	113.6	1.13	
2	Sunflower	106.2	115.8	3.90	
1	Sesame	106.6	115.4	10.70	
3	Maize	120.7	136.4	7.04	
1	Poppy	134.9	151.7	6.67	

The *saponification value* of genuine olive oil, according to De Negris and Fabris, who examined 203 samples, may range from 18.5 to 19.6%, and is usually 19.0. 106 samples examined by Oliveri had values ranging from 19.05 to 19.5, 38 Californian oils tested by Tolman and Munson ranged from 18.9 to 19.5, 400 samples of commercial oil (mostly Spanish and Italian) tested by the writer had values ranging from 18.80 to 19.29%, and 20 samples of oil from Tunis and Algeria ranged from 18.92 to 19.19%. A low saponification might be due to the presence of olive-kernel oil or to adulteration with rape, mustard, sperm, or mineral oil. No adulterant likely to be added would materially *raise* the saponification value of olive oil.

The *rise of temperature* on treating the sample *with sulphuric acid* (Maumené's test) or *with bromine* (Hehner and Mitchell's test) are valuable indications of the purity of olive oil. Almost all oils, except cocoanut olein and tallow and lard oils, produce more heat than olive oil, so that a rise of temperature of more than 45° with sulphuric acid (10 c.c. of acid containing 97% H_2SO_4 and 50 grm. of oil) may at once be considered as indicating probable adulteration, and in some cases it allows of an approximate estimation of the extent of the sophistication.

Archbutt[1] has determined the *heat of bromination* of 10 samples of olive oil and obtained results ranging from 13.55 to 14.5, using 1 grm. of oil and 1 c.c. of bromine. The thermal values when multiplied by 5.7 agreed very nearly with the iodine values.

The *elaidin test* is of little use unless carried out under standard conditions.[2] The reagent should be prepared by dissolving 6 grm. of mercury in 15.6 c.c. of nitric acid (1.42) in a 50 c.c. stoppered cylinder immersed in cold water, it should be mixed with the oil in the proportion of 1 part of reagent to 12 of oil by weight and the mixture kept at a fixed temperature and shaken every 10 minutes. Under these conditions, at 10°, genuine olive oil is converted into a solid pale yellow coloured mass of elaidin in about 1 hour, arachis oil rather more slowly, but rape, cottonseed, sesame, and other more strongly drying oils remain partially or wholly liquid and are coloured orange or red. To increase the delicacy of the test, it should be made at 25°. Olive oil will, then, take from 200 to 400 minutes to solidify, and 10% of more strongly drying oils if present will delay the solidification, darken the colour, and soften the consistency of the elaidin formed. It is said that as little as 5% of poppy oil can be detected by this test at 10°, which requires confirmation, but most adulterants are more readily detected by other tests. Olive oil which has become bleached by exposure to sunlight no longer forms a solid elaidin.

Useful information as regards the *oxidising properties* of an olive oil may be obtained by exposing 0.5 grm. on a watch-glass to the air in a water-oven at 100° for about 16 hours side by side with an equal weight of a standard sample on a watch-glass of the same curvature. Livache's or Bishop's tests (pp. 36 and 38) may also be used.

Reference to the tables on pp. 44–45 will show that the *oleo-refractometer* of Amagat and Jean is a valuable instrument for the rapid testing of olive oil, the recorded deviation of genuine samples ranging from 0° to + 3.5°. 106 samples examined by Oliveri[3] ranged from 0° to + 2°.

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[1] *J. Soc. Chem. Ind.*, 1897, **16**, 309.
[2] Archbutt, *J. Soc. Chem. Ind.*, 1886, **5**, 303.
[3] *J. Soc. Chem. Ind.*, 1894, **13**, 45.

All fixed oils likely to be added as adulterants would increase the refraction, except neat's-foot, arachis, lard, and tallow oils.

The *unsaponifiable matter* of genuine olive oil contains phytosterol, but no cholesterol. It does not exceed 1.5% in normal olive oils of the first and second pressing. In olive residuum oils (*les huiles de grignon d'olives*), however, and also in certain olive oils of the third pressing, larger quantities, even as much as 3.3%, of unsaponifiable matter have been found by the writer, derived, according to Milliau, from the shell of the olive nut. Any excess would probably include hydrocarbons from mineral or rosin oil, or wax alcohols from sperm or some other marine animal oil.

Cottonseed oil, unless it has been rendered insensitive by heating, would be detected by Halphen's colour test (page 135), the result of which must, however, be interpreted in conjunction with the quantitative values, especially the sp. gr., refractive power, iodine value, thermal tests, and the titer test of the mixed fatty acids, all of which would be raised by the addition of cottonseed oil. Some of these might be adjusted by the addition of a third oil, but the fraud would be detected by an abnormality somewhere if a complete examination were made. The addition of mineral oil or sperm oil, for instance, would increase the percentage of unsaponifiable matter. Other colour tests which may be applied are those with silver nitrate (*Bechi, Milliau*) and nitric acid (see under "Cottonseed Oil"). As some genuine olive oils have been found to give a brown colour in Bechi's test and a yellowish-brown colour with nitric acid, the results of these colour tests must be used with caution. A mixture of cottonseed and lard oils could be made having the normal sp. gr. and iodine value of olive oil, but the oleo-refractometer, the titer test of the mixed fatty acids, and the iodine value of the liquid fatty acids, would detect adulteration with such a mixture.

Sesame oil would be detected by the very delicate furfuraldehyde test (p. 143). Some genuine olive oils have been found to give a pale violet or rose-red colouration in this test, but it is unlikely for error to occur if proper consideration be given to the quantitative values. Sesame oil, if present, would affect the quantitative values very much in the same way as cottonseed oil.

Arachis oil can be detected in olive oil by Bellier's test (p. 99) and estimated by Renard's process (p. 93). The ordinary quantitative values of this oil are little different from those of olive oil. Some indications of its presence might be obtained by an abnormally high iodine value, but this would be very uncertain (recorded values for arachis oil, 83.3 to 105; for olive oil, 76.2 to 94.7). It may be noted that sesame oil is frequently mixed with arachis oil, and the two may, therefore, occur together. Arachidic acid occurs in *rape* and *mustard* oils, but these would betray their presence by lowering the saponification value and raising the iodine value and thermal values of olive oil.

Poppy oil or maize oil added to olive oil would affect the sp. gr., iodine values, and thermal values much in the same way as cottonseed oil, but they would not alter the titer test of the mixed fatty acids, nor increase the percentage of solid fatty acids as cottonseed oil would do. Poppy oil has a high iodine value and dries strongly. Maize oil is said to give a peculiar red colour when shaken with nitric acid (1.37), which is quite different from the colour obtained with cottonseed oil.

Lard oil in most of its quantitative values closely resembles olive oil, and would not be detected by the ordinary tests. The odour of the sample when warmed might reveal its presence, but the detection of cholesterol in the unsaponifiable matter by Bomer's test (see under "Cholesterol") would be the best evidence of the presence of lard oil. It might also be worth while to look for stearic acid in the mixed fatty acids by Hehner and Mitchell's process, since olive oil contains no stearin. Lard oil would increase the percentage of solid fatty acids.

Fish and other marine animal oils would probably show themselves by the taste, the smell on warming the sample, and the red colour produced on heating the oil with caustic soda solution. Most fish oils would raise the sp. gr. and iodine value, but they would be especially identified by the insoluble bromoglyceride formed by adding bromine to the solution of the oil in ether and acetic acid in Hehner and Mitchell's process (p. 28). **Linseed oil** would, of course, give a similar precipitate.

The characters of commercial olive oil must depend to some extent upon whether, in the process of expression or extraction, the olive kernels have been crushed and the *olive-kernel oil* included.

OLIVE-KERNEL OIL.

This oil was formerly believed to be quite different in properties from ordinary olive oil (the oil of the mesocarp), having a sharp and bitter taste, a dark green or brown colour, and being readily soluble in alcohol owing to the presence of much free fatty acid; but it has been shown by Klein[1] that the characters formerly assigned to olive-kernel oil were really those of *pyrene* or *bagasses* oil, the dark coloured, much decomposed oil expressed from the stones and refuse of the first and second pressings of the olives. Pure olive-kernel oil, prepared both by cold and warm expression from the kernels alone, without any admixture of the pulp, was found to have the following characters, as compared with a sample of *bagasses* oil:

	Olive-kernel oil	"Bagasses" oil
Sp. gr. at 15.5°	0.9186 to 0.9191	0.9277
Saponification value, %	18.23 to 18.38	19.05
Iodine value, %	86.99 to 87.78	71.57
Refractive index	1.4682 to 1.4688	
Free fatty acids, %	1.00 to 1.78	11.12

From these results it appears that pure olive-kernel oil is higher in sp. gr., somewhat higher in iodine value, and lower in saponification value than most olive oil, but it does not naturally contain an excess of free fatty acid.

In consequence of the belief prevalent among manufacturers and dealers that the presence of kernel oil in olive oil causes rapid decomposition of the latter to take place, Klein made mixtures of pure olive oil and pure olive-kernel oil and kept them in well-stoppered bottles, excluded from light, for 6 to 7 years. Scarcely any change took place either in the colour, taste, or smell of the oil, and the increase of free fatty acid was trifling in amount, proving that there is no reason why the stones and fruit of the olive should not be crushed together if the oil is properly refined immediately afterward.

Klein detected no arachidic acid in olive-kernel oil.

TEA-SEED OIL.[2]

(See also pp. 69.) This oil, obtained from the seeds of the tea plant, *Camellia theifera*, has long been used in China as an edible oil, for burning, and for soap-making. It resembles olive oil in general characters and forms a solid elaidin. Two varieties, Chinese and Assam, are recognised. Oil of Assam tea seed, grown in Java, ex-

[1] *Zeit. angew. Chem.*, 1898, 847.

[2] Schaedler, Technologie der Fette (1892) p. 579; *J. Soc. Chem. Ind.*, 1894, 13, 79.

amined by Italie, was a pale yellow thin oil, having an acrid taste and composed of palmitin, olein, and linolin, with traces of volatile acids, lecithin and phytosterol. A plant, *Camellia oleifera*, closely allied to the tea plant, is largely cultivated in China for the sake of the pale bland oil obtained from its seeds, which is said to be a very good lubricant for delicate machinery. It is dangerous for use as a food, unless refined, owing to the presence of saponin. The seeds of the Japanese *Camellia japonica* also yield an oil which is said to excel as a lubricant.

II. RAPE OIL GROUP.

Black Mustard Seed Oil.
Eruca Sativa Seed Oil.
Indian Mustard Seed Oil.
Jamba Oil.
Radish Seed Oil.
Rape Oil (Colza Oil).
Ravison Oil.
White Mustard Seed Oil.

BLACK MUSTARD OIL. WHITE MUSTARD OIL.

(See also p. 69.) These oils, obtained, respectively, from the seeds of *Brassica* (*Sinapis*) *nigra* and *Brassica* (*Sinapis*) *alba*, resemble rape oil in composition and general characters. The resemblance is closest in the case of white mustard oil, that of black mustard being higher than rape oil in sp. gr. and iodine value. A sample of crude mustard-husk oil (by-product from the manufacture of mustard from black and white seed mixed) examined by Archbutt gave the following results:

Sp. gr. at 15.5°	0.9203
Viscosity at 15.5°	Practically the same as that of rape oil.
Saponification value	173.1
Iodine value (Wijs)	116.9
Unsaponifiable matter, %	3.3
Free (oleic) acid, %	3.6
Maumené thermal test (50 grm. oil + 10 c.c. 97% H_2SO_4).	75.0°

A sample of mustard-husk oil examined by Hehner and Mitchell gave 1.5% of brominated glyceride insoluble in ether.

Mustard oil is used for soap-making, burning, and lubricating. In drying properties it resembles rape oil, and contains arachidic acid.[1] (See p. 316.)

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[1] Archbutt. *J. Soc. Chem. Ind.*, 1898, 17, 1009.

INDIAN MUSTARD OIL.

(See also p. 69.) Two samples of this oil, from the seeds of of *Brassica juncea*, a plant closely allied to *B. nigra*, were examined by Crossley and Le Sueur[1] and gave the results stated below. The oil is clear yellow in colour, and is largely used in India as an article of food and also medicinally. The first sample was from Bombay, variety "mustard," the second from Bengal, variety "rai."

Sp. gr. 15.5°	Saponification value	Iodine value	Reichert-Meissl value	Hehner value	Efflux time (seconds) of 50 c.c. at 70° F. Redwood	Butyro refractometer degrees at 40°	Optical activity in 200 mm. tube	Free (oleic) acid, %
0.9206	180.1	108.29	0.89	....	382.8	.....	−25′	0.94
0.9158	172.1	101.82	0.33	95.49	379.3	60.0	−18′	1.79

ERUCA SATIVA SEED OIL.[2]

(See also p. 69.) This oil is obtained from the seeds of a plant closely allied to the mustards, extensively cultivated in India, and is used there for burning and to some extent as a food. It is yellow in colour and has an odour of turnip or mustard. Crossley and Le Sueur describe it as a non-drying oil, but it probably resembles rape oil in this respect, as it does in general physical and chemical characters. The three samples examined gave results as follows:

Sp. gr. 15.5°	Saponification value	Iodine value	Reichert-Meissl value	Hehner value	Efflux time (seconds) of 50 c.c. at 70° F. Redwood	Butyro refractometer degrees at 40°	Optical activity in 200 mm. tube	Free (oleic) acid, %
0.9152	169.0	97.41	0.11	....	405.8	59.2	−11′	0.93
0.9165	174.1	99.10	0.77	....	369.4	....	−18′	0.63
0.9177	170.4	99.72	0.66	95.49	371.0	....	....	0.53

RADISH SEED OIL.

(See also p. 69.) This oil is obtained from the seeds of *Raphanus sativus*, or oil-radish. It resembles rape seed oil, and is used for the same purposes.

[1] *J. Soc. Chem. Ind.*, 1898, **17**, 992.
[2] Crossley and Le Sueur. *J. Soc. Chem. Ind.*, 1898, **17**, 992.

RAPE OIL. COLZA OIL.

(See also p. 69.) This oil is obtained from the seeds of several varieties of *Brassica campestris*, of the order Cruciferæ, cultivated extensively in France, Germany, Austria-Hungary, Roumania, S. Russia, India, China, and Japan. The oils yielded by the different varieties of seed, though botanically quite distinct, are similar in their chief physical and chemical characters, and are not distinguished commercially, being all sold as rape or colza oil.[1]

Rape oil is obtained from the crushed seed by expression or by extraction with solvents. The crude oil is yellowish-brown or brownish-green in colour, has a peculiar odour and somewhat pungent taste, and contains foreign matters which separate to some extent by keeping the oil, but cannot be wholly removed by passive treatment. These lessen the combustibility, cause much smoke during the burning, and also tend to promote decomposition of the oil, with liberation of free acid. To remove them, the crude or "brown rape oil" is usually refined by agitating it, while warm, with from 0.5 to 1.5% of strong sulphuric acid; and after the foreign matters and suspended acid have subsided, the oil is washed by agitation with steam and hot water. This process is simple and rapid, but it has the disadvantage that some hydrolysis of the esters takes place, increasing the amount of free fatty acid in the oil, which is detrimental to it as a lubricant; the refined oil is also liable to retain traces of free sulphuric acid. Rape oil intended for use as a lubricant is, therefore, preferably refined with fuller's earth. Refined rape oil is pale yellow in colour and has a characteristic taste and smell.

The following results were obtained with a consignment of Chinese rape seed oil, before and after refining on a large scale.

	Crude	Refined
Sp. gr. at 15.5°	0.9146	0.9147
Saponification value	172.1	171.9
Iodine value	101.1	101.0
Maumené thermal value	58.7°	57.8°
Unsaponifiable matter, %	1.65	1.20
Free (oleic) acid, %	0.4	1.4

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[1] For further particulars see Archbutt and Deeley. Lubrication and Lubricants, 107.

Rape oil stands between drying and non-drying oils. It does not thicken readily when heated and exposed to the air, and yet gives but an imperfectly solid elaidin with nitrous acid. In non-drying characteristics it is decidedly inferior to olive oil, but owing to its usually lower price, freedom from excess of acidity, and less tendency to decompose and become rancid, it is extensively used in admixture with mineral oils for engine and machinery lubrication, especially on railways. As an illuminant for railway carriages it has been almost superseded by gas and electricity, but it is still used very largely as a burning oil for other railway lamps and miners' safety lamps.

Rape oil has been found to contain esters of rapic and erucic acids,[1] but the high iodine value of the oil points to the presence also of an acid or acids of the linolic or linolenic series. Esters of saturated fatty acids occur in very small proportion[2] and include arachidic and, probably, lignoceric acids. Ponzio[3] found 0.4% of arachidic acid in one sample. Alén[4] found arachidic acid in the oil from Guzerat seed, but not in that from the European varieties. Archbutt[5] found 1.43% of arachidic (and lignoceric) acids in rape oil extracted by means of ether from Guzerat seed, and 1.14% in commercial (Stettin) rape oil expressed from rape and rubsen seed. Of 51 samples of commercial rape oil which were specially examined by Renard's process, about two-thirds were found to contain arachidic acid. Indian rape oil from *B. glauca* seems to contain more of this acid than the European oil, and the extracted oil more than the expressed oil; of the latter, the cold-pressed oil probably contains less than the hot-pressed.

Rape oil and other oils from the *Cruciferæ* are commonly stated to contain sulphur compounds and to give rise to silver sulphide on treating their ethereal solutions with a few drops of solution of silver nitrate in alcohol. If the oil is boiled with a 10% solution of pure potassium hydroxide, an immersed silver coin becomes blackened. Sulphur is present sometimes, but is accidental.

According to Schaedler, rape oil solidifies at -2° to -10°; but Holde states that all rape oils sooner or later solidify at 0°. The following experiment was made by Archbutt. Some genuine refined rape oil was placed in a glass tube, immersed in melting ice for 3 hours without

[1] Reimer and Will (*Ber.*, 1886, **19**, 3320) found in some casks of old rape oil, a tallow-like deposit consisting of di-erucin.

[2] Tolman and Munson found from a trace to 1.43% of solid fatty acids in 4 samples of rape oil, by Muter's method.

[3] *J. pr. Chem.*, 1893, **48**, 487.

[4] *Svensk. Kemisk Tidskrift*, 1893, 179.

[5] *Jour. Soc. Chem. Ind.*, 1898, **17**, 1009.

stirring, and then for 3 hours longer, stirring at intervals. It remained clear and fluid. Some of the same oil, previously frozen, having been added, the oil was kept in ice for 3 hours longer, with occasional stirring, but the frozen oil slowly melted. The temperature was then gradually reduced to −10 to −9°, and the oil became very turbid, but after remaining for 2 hours at this temperature, with stirring, it did not lose its fluidity. After still further reducing the temperature to −11.6°, and stirring, the oil solidified in about half an hour.

The chief physical and chemical constants of rape oil are given on p. 69, and the oleo-refractometer value on p. 44. Some constants of a number of Indian crude rape oils expressed from different varieties of pure seeds have been determined by Crossley and Le Sueur[1] and are given in the table on p. 126. The following results by Archbutt were obtained with rape oil extracted from the seed by ether in the laboratory:

	Yellow Guzerat seed oil	Brown Calcutta seed oil	Madras seed oil
Sp. gr. at 15.5°	0.9133	0.9146	0.9140
Saponification value	175.0	174.2	174.5
Iodine value	97.8	102.7	99.6

The following are some observed data from the mixed fatty acids of rape oil:

		Observer
Sp. gr. at 99°/15.5°	0.8438	Allen.
Sp. gr. at 100°/100°	0.8758	Archbutt.
Solidifying-point (titer test) colza oil	12.7–13.6	Lewkowitsch.
Solidifying-point (titer test) rape oil	11.7–12.2	Lewkowitsch.
Refractive index at 60° F.	1.4991	Thoerner.
Iodine value of mixed fatty acids	96.3–105.6	Various.
Iodine value of liquid fatty acids	124.2–125.5 120.7	Tortelli and Ruggeri. Wallenstein and Finck.

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[1] *J. Soc. Chem. Ind.*, 1898, 17, 989.

Assay of Commercial Rape Oil.—Owing to the enormous extent to which rape oil is used for lubricating and burning, the estimation of *free acid* is of great importance (see under "Olive Oil," p. 110). The method is described on p. 9.

According to Archbutt and Deeley,[1] commercial refined rape oil contains on an average about 2.2% of free acid calculated as oleic acid, ranging from 1% to about 6%, but seldom exceeding 4%. 378 samples, all representing large contracts, gave the following results:

Number of samples	Free (oleic) acid, %
122	1.1 to 1.9
223	2.0 to 2.9
30	3.0 to 3.9
3	4.0 to 5.7
378	Average, 2.21%

It is evident from these figures that carefully refined rape oil should not contain more than 3% of total acidity. The traces of free sulphuric acid in 3 samples of rape oil refined with this acid were determined and found to range from 0.0026 to 0.0056%, from which it is concluded that the percentage of free *mineral* acid in refined rape oil should not exceed 0.006% of H_2SO_4, which is equivalent to 0.035% of oleic acid.

Rape oil is subject to numerous adulterations, the more important of which can be detected with tolerable certainty.

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[1] Lubrication and Lubricants, p. 211.

INDIAN RAPE OILS. CROSSLEY AND LE SUEUR.

Botanical name	Variety	Locality	Sp. gr. at 15.5°	Saponification value	Iodine value	Reichert-Meissl value	Hehner value	Efflux time (seconds) of 50 c.c. at 70° F. Redwood	Butyro refractometer degrees at 40°	Optical activity in 200 mm. tube	Free (oleic) acid, %
Brassica campestris.....	red	N. W. Provinces...	0.9148	171.6	99.20	0.79	96.30	390.6	....	−7′	0.73
Brassica campestris.....	glauca......	N. W. Provinces...	0.9142	171.4	97.71	0.67	95.04	402.6	59.2	−10′	0.45
Brassica campestris.....	dichotoma..	N. W. Provinces...	0.9154	172.2	104.84	0.22	95.57	371.8	....	...	0.39
Brassica campestris.....	....	Punjab..........	0.9163	173.4	96.25	0.43	94.56	393.2	....	...	0.65
Brassica campestris.....	brown	Bombay	0.9171	172.8	94.10	0.00	....	464.6	....	...	1.00
Brassica campestris.....	yellow	Bombay	0.9141	169.4	96.66	0.00	....	413.8	....	−5′	0.36
Brassica campestris.....	napus	Bengal..........	0.9146	167.7	97.70	0.00	95.55	398.0	58.8	−15′	0.95

The *sp. gr.* of genuine rape oil averages 0.915 at 15.5°. Of 52 samples examined by Archbutt,[1] 7 had sp. gr. below 0.9140, 27 above 0.9139 and below 0.9150, and 18 above 0.9149 and below 0.9160. The lowest was 0.9132 and the highest 0.9159. 30 samples of brown rape oil, known to be genuine, examined by Sir Boverton Redwood, ranged in sp. gr. from 0.9145 to 0.9154, the average being 0.9149. The 7 samples of crude oil examined by Crossley and Le Sueur given on page 126 ranged in sp. gr. from 0.9142 to 0.9171, but from the abnormally high viscosity and low iodine value of the latter sample, it would appear to have become oxidised. 358 samples of the commercial oil more recently examined by Archbutt gave the following results:

	Number of samples
0.9136 to 0.9139	13
0.9140 to 0.9149	241
0.9150 to 0.9159	103
0.9160	1
	358

The average sp. gr. was 0.9147. The experience of Allen confirmed the results of Archbutt and Redwood, so that 0.9160 may be regarded as the maximum sp. gr. for genuine rape oil at 15.5°. North German (Baltic) rape oil is usually somewhat heavier and less pure than the French and Belgian products. The seed crushed in England, imported from the East Indies and all parts of Europe, gives an oil varying in sp. gr. from 0.9136 to 0.916. Black Sea rape (ravison) oil is an inferior, more strongly drying oil than that expressed from cultivated rape seed, and its presence in rape oil must, therefore, be regarded as adulteration.

The *sp. gr.* of rape oil is a valuable indication of its purity, as all the ordinary adulterants are heavier than the genuine oil, with the exception of mineral oil and sperm oil, which can be detected and estimated with accuracy by methods described on pp. 21 and 81. Foreign *seed oils* of more or less drying character, as sesame, sunflower, niger-seed, hempseed, cottonseed, or linseed oil, or possibly cocoanut olein, all range between 0.920 and 0.937. Hence, if the sample has a sp. gr.

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[1] *J. Soc. Chem. Ind.*, 1886, 5, 310.

of 0.918, it may possibly contain even 50% of these oils, while the smell and colour will be little affected. Seed and nut oils deteriorate rape oil by increasing its gumming properties, with the exception of arachis oil and cocoanut olein, and the addition of either of these is improbable. Arachis oil could be detected as in olive oil (page 117), due allowance being made for the arachidic acid naturally present in rape oil itself (see p. 123), and cocoanut olein would be indicated by the raised saponification value and reduced iodine value of the sample.

The *viscosity* of rape oil is a valuable indication of its purity, as it is moderately constant and exceeds that of any oil likely to be used as an adulterant. The sample should always be compared with a specimen of rape oil known to be genuine, or with pure glycerol diluted to 1.226 sp. gr. which at 15.5° has the same viscosity as average rape oil. The time of efflux of 50 c.c. from Redwood's viscometer at 70° F. should not be less than 370 seconds, and ranges from this up to about 415 seconds.[1] The number 464.6 recorded by Crossley and Le Sueur for Bombay rape oil is exceptionally high. The lowered viscosity of an adulterated oil could be corrected by the addition of castor or blown oil, but these would raise the sp. gr. and acetyl value. Heavy mineral oil would be found in the unsaponifiable matter.

The *saponification value* of genuine rape oil ranges from 170.0 to 175.0. A value in excess of 175.0 would indicate the presence of ravision or other more strongly drying oil. A lower value than 170.0 would indicate the presence of an unsaponifiable oil or sperm oil, or both. Refined rape oil has been frequently adulterated with a specially purified mineral oil. This addition interferes with the burning qualities of the oil, causing it to smoke and form much deposit on the wick.

The *iodine value* of rape oil ranges from 97 to 105%, being slightly less than that of cotton or sesame oil, and considerably below that of the more strongly drying oils. This test is useful for the detection of ravison oil, which has a higher iodine value than rape oil.[2]

The *Maumené thermal value*, or rise of temperature on mixing genuine rape oil (50 grm.) with sulphuric acid (10 c.c.) containing 97% of H_2SO_4, ranges from about 58° to 63°. An abnormally high result indicates ravison or other more strongly drying oil, and a low figure indicates mineral or sperm oil. Hehner and Mitchell's *bromine thermal test* (p. 60) may be used for the same purpose.

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[1] These numbers refer to an instrument which delivers 50 c.c. of water at 70° F. in 25.74 seconds.

[2] Milrath (*Zeitsch. öffentl. Chem.*, 1907, **19**, 371) obtained the following results with 3 samples of Austrian rape oil: Sp. gr., 0.9138 to 0.9155; refraction at 25°, 67.7 to 67.9; at 40°, 59.7 to 59.8; acid value, 3.1 to 7.2; saponification value, 173.1 to 174.3; iodine value, 106.9 to 108.2. These are exceptionally high iodine values.

The *melting and solidifying-points of the mixed fatty acids* of rape oil are raised by cottonseed and lowered by many other oils, such as ravison, linseed, or fish oils.

The *unsaponifiable matter* should not exceed 2%. In the expressed oil it is usually near 1%, but in rape oil extracted from the seed by petroleum spirit some allowance must be made for residual hydrocarbons. If more than 2% of unsaponifiable matter be found, it should be purified by resaponification; and if still in excess of 2%, the purified product should be further examined to ascertain whether mineral or rosin oil, cholesterol from animal oils, or wax alcohols from sperm oil are present. In genuine rape oil, the unsaponifiable matter consists mainly of phytosterol.

A simple and useful *oxidation test* may be made by exposing 1 grm. of the sample on a watch-glass to the air in a water-oven at 100° for about 16 hours, side by side with a sample of known purity; both samples being contained in watch-glasses of the same curvature. On examining the condition of the oils when cold, genuine rape oil of the best quality for lubricating will be found to be still quite fluid when caused to flow by inclining the glass, and will not have dried; inferior samples will have dried at the edges or have crept up and formed dry spots on the sides of the glass, and most rape oils will have thickened more or less considerably. Livache's test may also be used.

An abnormally low sp. gr. and viscosity of extracted rape oil is sometimes due to incomplete expulsion of the petroleum spirit used in the extraction process. Such oil will have an abnormally low *flashing-point*. When tested in the Pensky-Martens or Gray closed-test apparatus, normal rape oil usually flashes at 410° to 450° F. (210° to 232°). The writer has occasionally met with samples of extracted oil flashing at 180° F. and losing about 1% in weight in 1 hour when 1 grm. of the oil was heated in a platinum dish in the water-oven.

Valenta's acetic acid test (p. 62) gives very characteristic indications in the case of rape oil and may be found useful in certain cases.

Halphen's colour test for cottonseed oil and the *furfural test* for sesame oil should not be omitted. They may be relied upon to give negative indications with genuine rape oil. Both tests are very delicate and must only be used as confirmatory evidence. The amount of foreign oil present must be calculated from the quantitative values. Press-bags which have been used for cottonseed and afterward for rape seed may be the cause of traces of colour in Halphen's test.

Ravison and cottonseed oils are two of the commonest adulterants of rape oil. Both raise the sp. gr., saponification value and Maumené thermal value, and lower the viscosity. Ravison oil raises the iodine value, and lowers the m. p. of the fatty acids. Cottonseed oil does not appreciably affect the iodine value of the oil, but it raises the iodine value of the liquid fatty acids and raises also the m. p. of the oil and of its mixed fatty acids. Cottonseed oil can only be added to refined rape oil; if added to the crude oil, it causes it to become red when refined with sulphuric acid. Both ravison and cottonseed oils are more strongly drying oils than rape.

Linseed oil is a very objectionable adulterant of rape oil. It may be added before refining or by crushing the seeds together. It causes such a marked effect in raising the sp. gr., iodine value, thermal values with sulphuric acid and bromine, in lowering the viscosity of the oil and the m. p. of the mixed fatty acids, and in increasing the tendency of the oil to oxidize, that even a small admixture cannot fail to be detected. Linseed oil and fish oils are especially identified by means of Hehner and Mitchell's bromo-glyceride test.

Fish oils are recognisable by their peculiar taste and odour on warming, also by the colourations developed with caustic soda and sulphuric acid. They lower the viscosity in a marked degree, and affect the quantitative values much in the same way as linseed oil. *Train oil* is said to be best detected by agitating 100 drops of the oil with 1 of sulphuric acid, when the depth of the red colouration will follow the proportion of the adulterant present.

Hedge-mustard oil may be used for adulterating rape oil, which it closely resembles. The most characteristic test is said to be the production of a green colour when the oil is treated with a quantity of alcoholic potash insufficient for complete saponification, and the filtered liquor strongly acidified with hydrochloric acid.

JAMBA OIL.

The oil described under this name in the table on p. 69 is a kind of rape oil which is occasionally exported from Kurrachi. It closely resembles ordinary rape oil, but according to Lewkowitsch[1] behaves abnormally when an attempt is made to convert it into thickened or "blown oil."

BLACK SEA RAPE OIL. RAVISON OIL.

Oil expressed from the wild rape seed of the Black Sea district, largely exported from Odessa, known as ravison oil, is inferior in quality to, and cheaper than ordinary rape oil. It has a higher sp. gr., higher saponification and iodine values, lower viscosity, and more strongly marked drying properties than ordinary rape oil. The unacknowledged admixture of this oil with rape must, therefore, be regarded as adulteration. To prevent any possible dispute, it should be definitely excluded in contracts for rape oil. The chief physical and chemical characters of a few samples of this oil are shown in the following table:

Sp. gr. at 15.5°	0.9175 to 0.9217
Saponification value	177 to 181.3
Iodine value	109 to 122
Maumené thermal value	66° to 76°
Viscosity	About 6 to 13% lower than that of refined rape oil.
Sp. gr. of mixed fatty acids at $\frac{100^\circ}{100^\circ}$	0.880

III. COTTONSEED OIL GROUP.

Beechnut Oil.
Brazil-nut Oil.
Cameline Oil.
Cottonseed Oil.
Cress Seed Oil.
Madia Oil.
Maize Oil.
Pumpkin Seed Oil.
Sesame Oil.
Soja Bean Oil.
Wheat Oil.

BEECH OIL. BEECHNUT OIL.

(See also p. 70.) This oil is obtained from the kernels of the fruit of the common or red beech tree, *Fagus sylvatica*. It has a clear yellow colour, a peculiar odour, and faint flavour; when freshly drawn it has an acrid flavour, which disappears in time. It is used in France for cooking and as an illuminant. It does not readily become rancid.

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[1] Oils, Fats and Waxes, II, 221.

BRAZIL-NUT OIL.

(See also p. 70). This oil is obtained from the Brazil nuts of commerce, the produce of *Bertholletia excelsa*, a tree which flourishes in northern Brazil and Venezuela. It is a pale yellow oil, odourless and of pleasant taste, but easily turning rancid. It is used for culinary purposes when fresh, also for burning and soap-making.

CAMELINE OIL. GERMAN SESAME OIL.

(See also p. 70.) This oil is obtained from the seeds of *Camelina sativa* (*Myagrum sativum*), "Gold of Pleasure," a plant of the order *Cruciferæ*. According to Schaedler, it has a golden yellow colour, a sharp, peculiar taste and smell, and dries slowly. It is used for burning and for making soft soap. The cold-pressed oil is sometimes also used as an edible oil. Cameline oil is said to be used as an adulterant of rape oil, but would be readily detected by its higher sp. gr., iodine value and Maumené value. It is liable to be contained in linseed oil from East Indian seed, and may account for the low iodine value and inferior drying properties of some samples of that oil.[1]

COTTONSEED OIL.

(See page 70.) Cottonseed oil is now expressed in enormous quantities in the United States, on the continent of Europe, and in Great Britain, from the seeds of the different varieties of the cotton plant.[2]

Crude cottonseed oil has a sp. gr. ranging from 0.916 to 0.930. It contains in solution, often to the extent of 1 %, a characteristic colouring matter, which gives it a ruby-red colour, sometimes so intense as to appear nearly black. The crude oil gives a bright red colouration with strong sulphuric acid (page 41). The soap from crude cottonseed oil rapidly oxidises on exposure to air with production of a fine purple or violet-blue colouration.[3] This test is characteristic. The colouring matter causes the oil to produce stains, and it is removed by agitating the crude oil at the ordinary temperature with 10 to 15% of solution of sodium hydroxide of 1.06 sp. gr. when the alkali combines with the colouring matter and the free fatty acids of the oil. The mixture becomes filled with black flocks which deposit on standing,[1] and leave the oil but slightly coloured. The loss from refining is usually from 4 to 7.5%, but occasionally amounts to 12 or 15. Hence it is desirable, before purchasing crude cottonseed oil for refining, to ascertain by a laboratory experiment what the percentage of loss is likely to be. Frequently the treatment with alkali is only carried far enough to remove the greater part of the colouring matter, the oil being then boiled with a solution of bleaching powder and subsequently treated with dilute sulphuric acid. This method of treatment is economical, but the oil acquires an unpleasant taste and smell which cannot be removed. Hence chemical bleaching cannot be used for the oil which is required for edible purposes.

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[1] Lewkowitsch, Technology of Oils, II, 43.

[2] See Lewkowitsch. Oils, Fats and Waxes, II, 143.

[3] "Cottonseed blue" is stated by Kuhlmann to have the composition of $C_{17} H_{24} O_4$. It is amorphous; readily destroyed by oxidising agents; insoluble in water, diluted acids, and alkalies; sparingly soluble in carbon disulphide and chloroform, but more readily in alcohol and ether; and dissolves with purple colour in strong sulphuric acid. The unoxidised colouring matter of cottonseed oil has been examined by J. Longmore, who, in a communication to Allen, stated that it is a pungent golden-yellow product, insoluble in water, but soluble in alcohol and alkaline solutions, and precipitated from the latter on addition of acids. It dyes well and perfectly fast on both wool and silk.

Refined cottonseed oil is of a straw or golden-yellow colour, or occasionally nearly colourless. The sp. gr. usually ranges from 0.922 to 0.926 and the solidifying point from 1° to 10°. By subjection to cold and pressure a certain proportion of "stearine" is separated, the m. p. of the residual oil being correspondingly lowered. This refined oil is usually almost free from acid, and, when properly prepared, is of pleasant taste. It is extensively employed for edible and culinary purposes. It is now substituted for olive oil in some of the liniments of the *United States Pharmacopœia*, but its principal applications are *in soap-making and the manufacture of factitious butter*.

The solid esters of cottonseed oil consist mainly of palmitin, with a little stearin, the liquid contains olein and linolin.

Cottonseed oil is characterised by the high m. p. of its mixed fatty acids (38°) and by the colour tests described below. In the elaidin test it gives an orange-coloured semi-fluid mass. It is not itself very liable to sophistication, owing to its cheapness, but it is frequently employed to adulterate other oils. Most oils likely to be added to cottonseed oil would lower the m. p. of the fatty acids, linseed oil and whale oil would be found by Hehner and Mitchell's bromo-glyceride test. For the detection of maize oil see under "Maize Oil."

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[1] The deposit thus formed, consisting of colouring and albuminous matters, alkali, and partially saponified oil, is technically called "mucilage." It is decomposed with a slight excess of acid, and the resulting dark-coloured grease is heated to a temperature of 120° (250° F.) with concentrated sulphuric acid, which renders insoluble the colouring matters, etc., while the impure fatty acids rise to the surface. On distilling these with superheated steam, a mixture of fatty acids is obtained, which is separated into stearic and oleic acids by pressure. The "cottonseed stearin" thus obtained is employed for making soap and composite candles and for various adulterations.

For the detection of cottonseed oil in other oils, Halphen's colour test generally suffices, and a determination of the sp. gr., iodine value, Maumené thermal test, and melting- or solidifying-point of the mixed fatty acids will generally enable the proportion present in a mixture to be determined.

The unsaponifiable matter is usually near to 1% and contains phytosterol. The rise of temperature of 50 grm. of the oil with 10 c.c. of sulphuric acid (97% H_2SO_4) is about 75° to 81°. The viscosity at 15.5° is about 3/4 that of refined rape oil at the same temperature.

The following are some observed analytical data from the mixed fatty acids of cottonseed oil:

		Observer
Sp. gr. at 15.5°/99°	0.8467	Allen.
Sp. gr. at 100°/100°	0.8816	Archbutt.
Solidifying-point (titer test)	35.6°–37.6° [1]	Lewkowitsch.
	32.2°–32.7° [2]	
	33.3°–34.1° [2]	
	34.4°–35.2° [2]	
	28.1°–28.5° [3]	
Refractive index at 60°	1.4460	Thoerner.
Iodine value of mixed fatty acids	111–116	Various.
Iodine value of liquid fatty acids	142–152	Various.

Cottonseed stearin (*cotton oil stearin*) (see p. 133) is, properly speaking, the solid fat separated from cottonseed oil by cooling and pressing. It is a pale yellow fat, of butter-like consistency, and largely employed for the manufacture of butter substitutes. The article known in commerce as "cottonseed stearin" is usually impure stearic acid from cottonseed oil, obtained by the method given in the foot-note on page 133. The crude oil expressed from decorticated cottonseed is sometimes very rancid and semi-solid at the ordinary temperature from the separation of solid fatty acids in the free state. By pressure it would yield a product similar to that obtained by distillation.

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[1] Natural refined oil.
[2] Partly "demargarinated" oils.
[3] Winter oil.

Colour Tests for Cottonseed Oil.

Halphen's Colour Test.[1]—If cottonseed oil or oil containing it is heated with carbon disulphide, sulphur, and amyl alcohol, a characteristic red is produced, the intensity of which is not the same with all samples of cottonseed oil, but with the same sample is proportional to the quantity of cottonseed oil present. In making this test, 3 c.c. of the oil, 3 c.c. of amyl alcohol, and 3 c.c. of a 1% solution of sulphur in carbon disulphide are mixed in a small test-tube and heated in a bath of boiling water. With as little as 5% of cottonseed oil present, a distinct red is developed in from 15 to 30 minutes; the colour is more intense and more rapidly produced the greater the proportion of cottonseed oil. Less than 5% can be detected by longer heating, and especially if the colour is compared with that given by a pure sample of oil. This indication is not quite characteristic of cottonseed oil, but is given also by kapok and baobab oils,[2] to detect which Milliau recommends the following procedure: The oil is saponified and the mixed fatty acids are liberated, washed, and dried. 5 c.c. of the melted acids are mixed with 5 c.c. of a 1% solution of silver nitrate in absolute alcohol, shaken *cold* and allowed to stand. The presence of even 1% of kapok and baobab oils are said to cause a dark brown colouration after 20 minutes, while cottonseed oil causes no reduction until the mixture is warmed.

The nature of the chromogenetic substance in cottonseed oil is not known, but it is rapidly destroyed by heating the oil to 250°. Raikow[3] says heating with open steam has no effect, but superheated steam or simple heating to between 210° and 220° quickly destroys, and heating to 150° for several hours very gradually destroys, the active agent. This has been confirmed by others. The heated oil becomes darkened in colour and acquires a disagreeable flavour, hence would be less likely to be mixed with an edible oil or fat than with a lubricating oil. Fischer and Payne have also shown that cottonseed oil is rendered insensitive to the test by treatment with chlorine or sulphurous acid.[4] Hence a negative reaction in Halphen's test does not prove the absence of cottonseed oil, and a pink colour must not be considered a proof of its presence, unless the quantitative reactions afford evidence in support. It has been shown that the fat of animals which have been fed on cottonseed cake may give the colour indications of cottonseed oil. Thus lard from the fat of pigs, and butter from the milk of cows fed on cottonseed cake may give the test and yet be quite free from cottonseed oil.

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[1] *J. Pharm. Chim.*, 1897, **6**, (9), 390.
[2] Milliau. *Compt. rend.*, 1904, **139**, 807.
[3] *Chem. Zeit.*, 1899, **23**, 1025.
[4] *Zeitsch. Nahr. Genussm.*, 1905, **9**, 81.

Silver Nitrate Test.—This test, originated by Bechi,[1] depends upon the presence in cottonseed oil of a substance which gives a brown precipitate with silver nitrate. It may be applied to the oil or to the mixed fatty acids therefrom. Several modifications are in use. The method recommended by an Italian Government Commission in 1887,[2] which is substantially that of Bechi, requires the two following reagents:

A. Silver nitrate, 1 grm.; alcohol (98% by volume) 200 c.c.; ether, 40 c.c.; nitric acid, 0.1 grm.

B. Amyl alcohol, 100 c.c.; rape oil, 15 c.c.

10 c.c. of the oil to be examined are mixed in a test-tube with 1 c.c. of reagent A, and then shaken with 10 c.c. of reagent B. The mixture is next divided into two equal portions, one of which is immersed in boiling water for 15 minutes. The heated sample is then removed from the water-bath, and its colour compared with the unheated half. Presence of cottonseed oil is indicated by the reddish-brown colouration of the heated portion. Only the purest alcohol should be used, and the rape oil used should be "cold drawn," and only slightly coloured; it should be filtered in a hot-water oven before preparing the reagent. To guard against errors from impurity of the materials, a blank test should be instituted side by side with the actual test.

The part played by the rape oil in this test is explained, according to Bechi, by the fact that whereas fresh cottonseed oils give the silver nitrate indication without rape oil, old and rancid samples or their mixed fatty acids do not interact unless this oil be added. Many chemists consider the addition of rape oil unnecessary. Thus, in the official method of the Swiss Society of Analysts[3] a single reagent is used, which is prepared by dissolving 1 grm. of silver nitrate in 5 c.c. of water, adding 200 c.c. of alcohol, 40 c.c. of ether and 0.1 c.c. of nitric acid (1.42). 10 c.c. of the oil are heated for 15 minutes in boiling water with 3 c.c. of this reagent, and it is said that 1% of cottonseed oil, if present, will be detected. Petkow,[4] who recommends this method, states that the sensitiveness of Bechi's test depends upon the relative amount of silver nitrate used.

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[1] *Chem. Zeit.*, **11**, 1328.
[2] See *Analyst*, 1887, **12**, 170.
[3] *J. Suisse de Chim. et Pharm.*, **35**, 448.
[4] *Zeit. öffentl. Chem.*, 1907, **13**, 21.

Milliau[1] prefers to operate upon the mixed fatty acids, but in preparing these regard must be had to the fact that prolonged heating of the acids at 100° or washing them by boiling with water must be avoided, as both cause a loss of the reacting body.[2]

This is probably the reason why some chemists have concluded that Milliau's test is less delicate than Bechi's. The following is the method of procedure recommended by Archbutt: Approximately 5 grm. of the oil are saponified, and the fatty acids are liberated from the soap solution by dilute sulphuric acid in a separating funnel and dissolved by shaking with about 70 c.c. of ether. The ethereal solution, after drawing off the aqueous liquid, is well washed with small quantities of cold water and poured through a dry filter into a dry flask. The ether is distilled off, and the fatty acids are heated on the steam bath for about 5 to 10 minutes to drive off the remaining traces of ether and water, and at once dissolved by pouring 20 c.c. of absolute alcohol into the flask. The solution is transferred to a 1-in. diameter test-tube and raised to boiling, then 2 c.c. of a 30% aqueous solution of silver nitrate are added and the test-tube is shaken and held over a white tile. In the presence of 5% of cottonseed oil a characteristic brown turbidity is produced almost immediately. If there be no immediate colouration, the solution is kept under observation for a minute or two at boiling heat by moving the tube to and fro from the tile to the flame, and if only 2% of cottonseed oil be present a distinct brown colouration will be obtained, though more slowly developed.

This test has been examined by a large number of chemists and is known to be given only by cottonseed, kapok, and baobab oils. To distinguish the two latter from cottonseed oil, see under "Halphen's Colour Test." Some genuine rape oils appear to reduce the silver nitrate very slightly, but the reaction takes place slowly and the colour produced is blackish, while with cottonseed oil it is brown. It has also been observed that some olive oils give a brown colour in Bechi's test. Fats which have been exposed to the air or have become rancid may reduce the silver solution owing to the presence of aldehydic compounds. Thus Bevan[3] found that lard which had been exposed to the air for some days gave Bechi's test, while some taken from the interior of the mass had no reducing property. It has also been shown that genuine butter and lard from animals fed on cottonseed oil may give this reaction. On the other hand, Bechi's test, like Halphen's, is not given by cottonseed oil which has been heated to 250°, and all cottonseed oils do not respond to the test to the same extent. Therefore, this test is no more certain than Halphen's and can only be used as an auxiliary to the quantitative reactions.

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[1] *J. Amer. Chem. Soc.*, 1893, **15**, 153.
[2] Archbutt and Deeley. Lubrication and Lubricants, p. 290.
[3] *Analyst*, 1894, **19**, 88.

It should be noted that Tortelli and Ruggeri[1] state that by applying this test to the fatty acids from the lead soaps soluble in ether, cottonseed oil which has been heated to 250° long enough not to respond to the ordinary test may still be detected. 5 grm. of the oil are saponified with 30 c.c. of alcoholic potassium hydroxide (60 grm. of the hydroxide in 1000 c.c. of 90% alcohol), the solution exactly neutralised with 10% acetic acid and poured in a thin stream into a hot solution about 300 c.c. in volume containing 5 grm. of lead acetate. The washed and dried lead soaps are warmed for about 20 minutes with anhydrous ether under a reflux condenser, and the ethereal solution, when cold, is filtered into a separating funnel and decomposed by shaking with dilute hydrochloric acid. After separating the aqueous liquid and well washing the ethereal solution with cold water, the ether is distilled off and the residual fatty acids are dissolved in 10 c.c. of 90% alcohol and 1 c.c. of a 5% aqueous solution of silver nitrate. The liquid is transferred to a test-tube and placed in water at 70° to 80°. It is stated that 1% of cottonseed oil can be detected in olive oil by heating for 2 minutes, and by heating for several hours 10% of oil which had been heated to 250° for 20 minutes could still be detected.

Nitric Acid Test.—This test is given in the form recommended by Lewkowitsch.[2] A few c.c. of the oil are vigorously shaken in the cold with an equal volume of nitric acid of sp. gr. 1.375 and then allowed to stand. Cottonseed oil gives an immediate coffee-brown colouration, which becomes very intense on standing, and mixtures of other oils with cottonseed give a similar brown colour. Stronger acid gives less definite results. The only advantage this test has over Halphen's test is that the brown colour is still given by cottonseed oil which has been heated so as to no longer respond to the latter test; on the other hand, Lewkowitsch states that he has met with many American cottonseed oils which have given with nitric acid such a faint colouration that 10% of these in olive oil could not be detected.

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[1] *Annali. dil. Laboratoria. Chim. de Gabelle.*, 1900, 4, 249.
[2] Oils, Fats and Waxes, II, 163.

In applying this test to a sample of oil, the colour obtained should be compared with that given under the same conditions with a pure sample of the same kind of oil, and this pure sample should, if possible, be an oil of the same commercial variety as the one under test. Mixtures of the oil with different proportions of cottonseed oil should also be tested. The test is most useful in the case of olive oil, most samples of which, when pure, are scarcely altered in colour by the nitric acid, or at the most give a light brownish-green or brownish-yellow colour on standing. But there are some olive oils which give a darker brown and yet give no other indication of the presence of cottonseed oil. It must also be borne in mind that many genuine rape oils give a brown colour with nitric acid, one such sample tested by the writer when mixed with olive oil in the proportion of 20% gave a brown colour in forty minutes which could not be distinguished from the colour given by 20% of cottonseed oil. Coste and Shelbourne[1] have thrown doubt upon this test for cottonseed oil in neat's-foot oil, as some pure samples of the latter also gave a brown colour on standing. It is, therefore, evident that great caution and much experience is needed in drawing conclusions from the result of this test, which may nevertheless prove useful in certain cases.

CRESS SEED OIL.

(See p. 70.) This oil is obtained from the seed of the garden cress, *Lepidium sativum.* It has a brownish-yellow or orange colour, and peculiar disagreeable smell. It is used for burning and soap-making (Schaedler).

MADIA OIL.

(See p. 70.) This oil is obtained from the seeds of *Madia sativa*, a native of Chili. It has a deep yellow colour and dries slowly. It is used for burning and soap-making.

MAIZE OIL. CORN OIL.

(See also p. 70.) Maize oil is expressed from the fruit germs or embryos of maize or Indian corn, *Zea mais*, which are separated from the grain in the manufacture of starch or after malting. The oil has a pale yellow or golden-yellow colour and an odour of maize meal or malt. It is a semi-drying oil, rather more strongly drying than cottonseed oil,[1] but much less so than linseed oil. It is, therefore, unsuitable either for lubricating or for mixing with paint. It is used to some extent as an edible oil and for burning, but its proper use is for soap-making. It makes an excellent soft soap, pale, and as free as can be from objectionable odour.

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[1] *J. Soc. Chem. Ind.*, 1903, 22, 778.

The sp. gr. of maize oil ranges from 0.921 to 0.928 at 15.5°. It solidifies at $-10°$ (Schaedler); below $-20°$ (Smith[2]); $-36°$ (Hopkins[3]); but deposits solid fat on standing, even at the ordinary temperature (Lewkowitsch[4]). It dissolves in 50 volumes of absolute alcohol at 16°. The absolute viscosity at 15.6° is 0.789[5] (viscosity of cottonseed oil, 0.82 to 0.91). The oil does not form a solid elaidin. In Maumené's test, the rise of temperature ranges from about 81 to 89°.

Maize oil is chiefly composed of olein and linolin, with a small proportion of saturated esters.[6] The high Reichert value, 4.2, found by Vulte and Gibson[7] proves the presence of volatile acids, and may help in the detection of maize oil in mixtures. The unsaponifiable matter ranges from about 1.4 to 1.7% and contains, according to Gill and Tufts,[8] sitosterol, the acetate of which melts at 127.1°. As the phytosterol acetate prepared from cottonseed oil phytosterol was found to melt at 120° to 121°, Gill and Tufts have proposed to make use of this difference for the detection of maize oil in cottonseed oil. From 1.1 to 1.5% of lecithin has been found in maize oil.

Maize oil is more likely to be used as an adulterant of other oils than to be itself adulterated. It gives no colouration with Halphen's reagent or with furfural; the presence of cottonseed oil or sesame oil could, therefore, readily be detected, unless the cottonseed oil had been heated. In the latter case, the raised m. p. and solidifying-point (titer test) of the mixed fatty acids would indicate cottonseed oil. Fish oils would be indicated by the bromoglyceride test and the odour on warming the sample.

The following are some data obtained by examination of the mixed fatty acids from maize oil:

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[1] Archbutt, *J. Soc. Chem. Ind.*, 1899, **18**, 346.
[2] *J. Soc. Chem. Ind.*, 1892, **11**, 504.
[3] *J. Amer. Chem. Soc.*, 1898, **20**, 948.
[4] Oils, Fats and Waxes, II, 131.
[5] Archbutt, *J. Soc. Chem. Ind.*, 1899, **18**, 346.
[6] *J. Amer. Chem. Soc.*, 1898, **20**, 948.
[7] *J. Amer. Chem. Soc.*, 1900, **22**, 453.
[8] *J. Amer. Chem. Soc.*, 1903, **25**, 251.

		Observer
Sp. gr. at 100°	0.8529	Winfield.
Titer test	19.	Lewkowitsch.
Iodine value	112–129	
Iodine value of the liquid fatty acids	136–144	

PUMPKIN-SEED OIL.

(See p. 70.) This oil is largely used for culinary purposes in Austria and Hungary, and ranks there next to olive oil in price. It is obtained from the seeds of the common gourd or pumpkin, *Cucurbita pepo*. The cold-expressed oil prepared by Poda[1] was greenish, with faint red fluorescence; that prepared by roasting and subsequent hot expression, as on a commercial scale, was brownish-green with deep red fluorescence. It easily becomes rancid, and has considerable drying properties. As a result of the examination of several commercial samples, as well as of genuine samples expressed by himself, Poda gives the following limits for the genuine oil:

Sp. gr.	0.923 –0.925
Iodine value	122.76 –130.68
Saponification value	188.4 –190.2
Butyro-refractometer, 25°	70.0 –72.5
M. p. of fatty acids, commenced	26.5 –28.5
M. p. of fatty acids, ended	28.4 –29.8

Linseed, sesame, cottonseed, and rape oils are said to be used as adulterants.

SESAME OIL. TEEL OIL. GINGILI OIL.

(See p. 70). Sesame oil, sometimes called benne oil, but distinct from the oil of *ben* or *behen*, is pale yellow, usually of a deeper hue than almond oil, nearly odourless, and has a bland and agreeable taste. That expressed from the seeds congeals at about —5°, but that extracted by solvents at about +5°. It is used as an edible oil, in cookery, and in the manufacture of margarine, it being compulsory in Germany and Austria to add 10% of it to butter substitutes to facilitate their detection when used to adulterate butter. In Belgium, 5% must be added (Lewkowitsch). Sesame oil is used in pharmacy and perfumery, for soap-making, and for adulterating almond and olive oils. It is also commonly mixed with arachis oil. It dries more strongly than rape oil, but much less than cottonseed oil, and does not readily turn rancid. "German sesame oil" is a name sometimes given to cameline oil.

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[1] *Zeitsch. Nahr. Genussm.*, 1898, 625.

Sesame oil contains olein, linolin, palmitin, and stearin, but its composition is not fully known. The unsaponifiable constituents, amounting to about 1.0 to 1.4% (Lewkowitsch), include phytosterol, 0.2 to 0.5% of a strongly dextrorotatory substance, "sesamin," and a phenolic body, "sesamol," which gives a brilliant red colouration with furfural and hydrochloric acid, by means of which sesame oil can be identified. Sesamol exists in the oil as a complex compound, from which it is liberated by an acid.[1]

Sesame oil is dextrorotatory, and in the absence of castor, croton, and rosin oils, this property may assist in its detection. The following observations have been published:

	Rotation in 200 mm. tube at 13° to 15°
Bishop,[2] 6 samples	+3.1 to +9.0
Rakusin,[3] 3 samples	+1.9 to +2.4
Utz,[4] 3 samples	+0.8 to +1.6
Sprinkmeyer and Wagner,[5] 3 samples	+1.03 to +1.42

The chief physical and chemical constants of this oil are given on page 70 and the oleo-refractometer value on page 45.

The mixed fatty acids have given the following figures:

		Observer
Solidifying-point (titer test)	21.2°–22.9°	Lewkowitsch.
	22.9°–23.5°	Lewkowitsch.
	23.7°–23.8°	Lewkowitsch.
Refractive index at 60°	1.4461	Thoerner.
Iodine value of mixed fatty acids	109–112	Various.
Iodine value of liquid fatty acids	126–140	

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[1] Compare Villavecchia and Fabris, *Zeit. angew. Chem.*, 1893, **17**, 505; Bomer, *Zeit. Nahr. Genussm.*, 1899, **2**, 705; Kreis, *Chem. Zeit.* 1903, **27**, 1030 and 1904, **28**, 956; Canzoneri and Perciabosco, *Gazzetta*, 1903, **33**, 253; and Malagnini and Armanni, *Chem. Zeit.*, 1907, **31**, 884.

[2] *J. Pharm. Chim.*, 1887, 300.

[3] *Chem. Zeit.*, 1906, **30**, 143.

[4] *Pharm. Zeit.*. **45**, 490.

[5] *Zeit. Nahr. Genussm.*, 1905, **10**, 347.

Comparative examinations of African, Indian, and Levantine sesame oils have been published by Utz[1] and by Sprinkmeyer and Wagner,[2] some of whose results are collected in the following table:

	African		Indian		Levantine	
	U.	S. & W.	U.	S. & W.	U.	S. & W.
Sp. gr. 15.5°	0.9232	....	0.9218	......	0.922	......
Rotation, 200 mm., 15°	+1.6°	+1.42°	+1.4°	+1.03°	+0.8°	+1.11°
Butyro-refractometer degrees, 25°	67.5	69.2	66.2	68.2	67.0	68.0
Butyro-refractometer degrees, 40°	59.5	......	58.2	......	59.1	......
Iodine value	106.3	114.11	104.8	108.31	107.7	108.84
M. p. of mixed fatty acids	24.6°– 24.8°	....	24.2°– 24.8°	....	24.6° 24.7°	....
Butyro-refractometer degrees of mixed fatty acids, 25°	53.2	......	53.5	......	54.0	......
Butyro-refractometer degrees of mixed fatty acids, 40°	45.0	......	47.2	......	45.1	......
Iodine value of liquid fatty acids	....	132.7	......	127.2	.....	126.3

Utz found that African oil gave the strongest furfural and stannous chloride reactions, and Indian the weakest.

The iodine values of 37 samples of sesame oil pressed from seeds of various origins were found by Wijs to range from 106.1 to 116.8; the oils from the "second pressings" gave values ranging from 105.2 to 110.3, and the "third pressings" from 103.9 to 109.8.[3]

Colour Tests.

Furfuraldehyde Test.—Sesame oil contains a substance ("sesamol," see above) which produces a rose-red colouration when the oil is shaken with cane-sugar and hydrochloric acid (Camoin, Baudouin). 0.1 grm. of cane-sugar is dissolved in 5 c.c. of cold hydrochloric acid (1.16), 10 c.c. of the oil are added, the tube is corked, shaken for 10 minutes, and allowed to stand. If only 2% of sesame oil be present, the acid which separates will be pink. If 5% or more be present, the emulsion will become pink while being shaken. Villavecchia and Fabris found this colouration to be caused by *furfural*, produced by the action of the acid on the sugar, and they have modified the test by using a solution of furfural instead of sugar. As furfural itself gives a violet colouration with hydrochloric acid, a very small quantity only must be used.

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[1] *Pharm. Zeit.*, 45, 490.

[2] *Zeit. Nahr. Genussm.*, 1905, 10, 347.

[3] *Zeits. Nahr. Genussm.*, 1902, 5, 1150.

A 2% solution of furfural in alcohol is prepared. 0.1 c.c. of this solution is placed in a test-tube, 10 c.c. of hydrochloric acid (1.16) and 10 c.c. of the oil are added, the tube is then corked, shaken for half a minute and allowed to stand. If only 1% of sesame oil be present, the acid which separates has a pink colouration; with 5%, a strong rose-red colour is obtained. This test is recommended, as it is simpler than that with sugar, and half a minute's shaking is quite sufficient. Wauters suggests pouring the oil on the reagent, and says that less than 1% can be detected by a crimson colour at the point of contact.

Lehnkering,[1] in examining a series of pure sesame oils, found some which, while of normal iodine value and refractive index, gave only feeble colours in the furfural test, not more than 1/10 as much colour as was given by the oils which reacted most strongly. Oils extracted from the seeds with ether gave colours ranging in intensity from 5 to 8 on the same scale.

Rancid oils may give a brownish tint in the Baudouin test, which will mask the reaction when only small amounts of sesame oil are present. Sprinkmeyer[2] found that rancid cottonseed oil containing sesame oil gave no red colour unless at least 17% of sesame oil were present. This shows the importance of using fresh cottonseed oil in testing margarine, which, according to German law, must contain sufficient sesame oil to give a distinct red colouration when 0.5 c.c. of the clear melted fat is mixed with 9.5 c.c. of cottonseed oil and shaken with hydrochloric acid and furfural as directed above. Kreis[3] states that rancid sesame oil gives a less intense colouration than fresh oil. Ambühl obtained an indigo-blue colour in applying the Baudouin test to some old rancid sesame oil. Kreis[4] thinks this must have been a mixture of the red colour due to furfural with the green colour obtained in Bishop's test. Bishop[5] found that fresh sesame oil gave no colour when shaken with 1.5 times its volume of hydrochloric acid

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[1] *Zeit. öffentl. Chem.*, 1903, **9**, 436.
[2] *Zeit. Nahr. Genussm.*, 1908, **15**, 20.
[3] *Chem. Zeit.*, 1908, **23**, 87.
[4] *Chem. Zeit.*, 1899, **23**, 802.
[5] *J. Pharm. Chim.*, 1889, **20**, 244.

(1.19), but if exposed to air and light for a few days it coloured the acid green. Oil which had been exposed for years coloured the acid almost blue, and a blue colouring matter separated on standing, the acid becoming green again. This reaction may, therefore, modify the colour obtained in the Baudouin test with old sesame oils, but it is stated that the oil which separates from the green- or blue-coloured hydrochloric acid will give the red colour on being shaken with hydrochloric acid and furfural.

Several observers have found that in applying the furfural test to certain olive oils of undoubted purity the acid liquid assumes a violet colouration after a short time; da Silva[1] found Douro olive oil gave this colour. It has also been observed that some genuine Italian, Tunisian and Algerian olive oils give a rose colouration, similar to that produced by about 5% of sesame oil.[2] According to Milliau, this is caused by a colouring matter derived from the aqueous part of the pulp of the fruit, and if the test be applied to the mixed fatty acids instead of to the original oil any possibility of error is obviated. Therefore, Milliau's modification should be adopted in cases where doubt exists as to the cause of the colouration.

Soltsein's Test.—The oil is mixed with an equal volume of stannous chloride solution, German Pharmacopœia strength, shaken vigorously (once only), and placed in boiling water. A red colouration is produced in the presence of sesame oil. This reaction is said to be more delicate than Baudouin's, and to be specially applicable to butters and margarines artifically coloured with coal-tar dyes, which are reduced and rendered colourless. As the delicacy of the reaction is impaired if the liquids remain too long in contact without separating, Soltsein recommends diluting the oil with twice its volume of petroleum spirit, adding half the volume of stannous chloride, shaking well, and standing the tube in water at about 40°.

Tocher's Test.—15 c.c. of the oil are shaken for about 30 seconds with a freshly made, practically colourless solution of 1 grm. of pyrogallol in 15 c.c. of concentrated hydrochloric acid (1.16). The aqueous liquid is drawn off through a wet filter-paper and heated for 15 minutes on a water-bath. In the presence of sesame oil it becomes coloured reddish-purple, appearing red by transmitted, and blue by reflected light. The test is very delicate, and will readily detect 2%

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[1] *Bull. Soc. Chim.*, 1898, **19**, 88.

[2] Villavecchia and Fabris, *Zeit. angew. Chem.*, 1892, 509.

of sesame oil in rape or olive oil. Bellier says this reaction is not given by certain genuine olive oils which give a red colour in the furfural test.[1]

Adulteration with *rape oil* would lower the sp. gr. and saponification value of sesame oil and the melting- and solidifying-points of the fatty acids.

Poppyseed oil would raise the iodine value and thermal tests, and also the refractometer numbers. It would lower the melting- and solidifying-points of the mixed fatty acids.

Cottonseed oil, unless it has been altered by heating, would be indicated by Halphen's test. It would raise the melting- and solidifying-points of the mixed fatty acids and would tend to raise the iodine value of the liquid fatty acids, sesame oil acids absorbing from 126.3 to 139.9 and cottonseed oil acids from 141.9 to 151.7% of iodine. Cottonseed oil would increase the rise of temperature in the thermal tests. It would not materially alter the other values. The mixed fatty acids of cottonseed oil were found by Farnsteiner[2] to contain rather more linolic acid than those of sesame oil, he having obtained tetrabromides corresponding with 18.5% of linolic acid from the former and 12.6 to 15.8% from the latter. But a larger number of samples need investigating.

Arachis oil would be detected and determined by isolating its arachidic acid.

SOJA-BEAN OIL.

This oil is obtained from soja or soy beans, the seeds of *Soja japonica* (*Soja hispida*), a plant native to China, Manchuria, Korea, and Japan, but also grown elsewhere. It has marked drying properties and, according to De Negri and Fabris, readily solidifies. The values on p. 70 are based upon the results of Morawski and Stingl, De Negri and Fabris, and Shukoff. Four commercial samples of Chinese bean oil examined by Korentschewski and Zimmermann,[3] one obtained direct from the factory in Kharbin, gave the following results, some of which are quite different from those previously recorded by the other observers. The oil is described as dark brown, having a faint odour suggesting tung oil, and a bland taste.

[1] *Ann. Chem. Anal.*, 1899, **4**, 217.

[2] *Zeit. Nahr. Genussm.*, 1899, **2**, 1.

[3] *Chem. Zeit.*, 1905, **29**, 777.

Sp. gr. at 15°	0.9264 to 0.9287
Solidifying-point	−14.6° to −15.3°
Saponification value	207.9–212.6
Hehner value	93.6–94.28
Iodine value	114.8–137.2
Maumené value	102°–116°
Acid value	1.86–15.46
Solidifying-point of mixed fatty acids	16°–17.3°
M. p. of mixed fatty acids	20°–21°

A sample of the crude commercial oil extracted from the beans in this country, examined by the reviser, in August, 1908, had a yellowish-brown colour, a somewhat pungent odour suggestive of crude mustard or rape oil, and gave the following results:

Sp. gr. at 15.5°	0.9254
Solidification-point	−10°
Saponification value	184.0
Iodine value	119.9%
Halphen's test	Negative

Soy beans are now being imported into Europe in large quantities from Manchuria, about 400,000 tons having been shipped to the United Kingdom during March to November, 1909. The beans contain about 17 to 18% of oil and, being rich in albuminoids and carbohydrates, have a high feeding value. The following further analyses by Archbutt show the character of the oil now being put on the market (1909). The oil is used for soap making.

	Unrefined	Unrefined	Refined
Sp. gr. at 60° F.	0.9256	0.9250	0.9226
Solidification-point	−16°	....	....
Saponification value	190.5	189.7	188.6
Iodine value	139.3	138.9	136.1
Unsaponifiable matter, %	1.54	1.27	1.30
Free (oleic) acid, %	0.3	0.5	1.2

WHEAT OIL.

(See p. 70.) Wheat oil is obtained from the germs of wheat, *Triticum*, by extraction with petroleum spirit. A yellowish-brown oil is thus obtained, having an odour of wheat. It easily becomes rancid. Frankforter and Harding[1] found in this oil from 2.4 to 2.6%

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[1] *J. Amer. Chem. Soc.*, 1899, **21**, 758.

of unsaponifiable matter which, as in the case of maize oil, contains sitosterol.[1] About 2% of lecithin was also found. The viscosity of the oil at 20° was 2.57 times that of rape oil at the same temperature. The refractive index at 20° was 1.4832. De Negri[2] obtained the following results from the mixed fatty acids:

Solidifying-point	29.7
Iodine value	123.3

IV. LINSEED OIL GROUP.

Candle Nut Oil.
Cedar Nut Oil.
Hempseed Oil.
Lallemantia Oil.
Linseed Oil.
Niger Seed Oil.
Pine Nut Oil.
Poppyseed Oil.
Safflower Oil.
Sunflower Oil.
Tung Oil.
Walnut Oil. Nut Oil.

CANDLE NUT OIL.

(See also p. 70.) This oil is obtained from the seed-kernels of *Aleurites moluccana* (*A. triloba*), a tree which flourishes over the whole of the South Sea Islands. The cold-pressed oil is almost colourless, or slightly yellow, of an agreeable flavour and smell, and is used as an edible oil. The hot-pressed oil has a brownish-yellow colour and unpleasant flavour, and is used for technical purposes.[3] It dries less rapidly than linseed oil and is used for mixing paints and making oil-varnishes.[4] It is obtainable in enormous quantities, and may be employed as an adulterant of linseed oil (Lewkowitsch[5]). The published iodine and saponification values of this oil vary considerably, as is shown in the following table:

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[1] Burian, *Monatsh.*, 1897, **18**, 551.
[2] *Chem. Zeit.*, 1898, **22**, 976.
[3] Schaedler, Technologie der Fette, p. 663.
[4] Spon's Encyclopedia, IV, 1393.
[5] Technology of Oils, II, 69.

	De Negri[1]	Lewkowitsch[2]	Kassler[3]	Fendler[4]	Imp. Inst.[5]
Sp. gr. at 15°	0.920a, 0.926b	....	......	0.9254	0.9274
Sp. gr. at 15.5°	....	0.9256	0.9248	......	......
Butyro-refractometer, 25°	....	76	......	......	......
Saponification value	184a, 187.4b	192.6	189.5	194.8	204.2
Iodine value	136.3a, 139.3b	163.7	152.8	114.2	139.7
Reichert-Meissl value	....	....	......	1.2	......
Acetyl value	....	9.8	......	......	......
Unsaponifiable matter, %	....	....	0.53	......	......
Mixed Fatty Acids.					
Solidifying-point	13°	....	12.5°	15.5°	......
Solidifying-point (titer test)	....	....	......	......	17.8
Iodine value	142.7a, 144.1b	....	157.5	......	......
Iodine value of liquid fatty acids.	....	185.7	......	......	......
	Extracted from the seeds by (a) petroleum spirit, (b) ether.	Extracted from kernels of nuts of A. moluccana (South Sea Islands).	Oil from Fiji.	Extracted by ether from seeds of A. moluccana from the Cameroons.	Extracted from the kernels of Chinese A. triloba.

Walker and Warburton[6] obtained from 7.28 to 8.21% of brominated glycerides by Hehner and Mitchell's process from the sample examined by Lewkowitsch.

A sample of the commercial oil, described as Lumbang oil, recently examined by the reviser, was light brown in colour, had an unpleasant and somewhat pungent odour, and gave the following results:

Sp. gr. at 15.5°	0.9252
Saponification value	193.6
Iodine value	154.6

The oil dried nearly as rapidly as linseed oil, and had about half the viscosity of rape oil at 15.5°. It contained 23.6% of free (oleic) acid. The saponification and iodine values agree with those observed by Lewkowitsch and Kassler.

CEDAR NUT OIL.

(See p. 70.) The commercial oil is expressed from the seeds of the Siberian cedar, *Pinus cembra;* it is golden-yellow, and of agreeable, though somewhat rancid taste. It contains the glycerides of linolic and oleic acids, the former predominating, a very little linolenic acid is also present; among the solid fatty acids palmitic acid has been identified, and there is also present a considerable proportion of volatile fatty acids.

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[1] *Oesterr. Chem. Zeit.*, 1898, 1, 202.
[2] Technology of Oils, II, 67.
[3] *Seifenseider Zeit.; Farben-Zeit.*, 1903, 8, 359.
[4] *Zeit. Nahr. Genussm.*, 1903, 1025.
[5] *Bull. Imp. Inst.*, 1907, 5, 135.
[6] *Analyst*, 1902, 27, 237.

A specimen of this oil examined by von Schmoelling[1] gave the following results:

	Oil	Mixed fatty acids
Sp. gr. at 15°	0.930	....
Solidifying-point	....	11.3°
Saponification value	191.8	....
Iodine value (Waller)	159.2	161.3
Hehner value	91.97	....
Volatile fatty acids	3.77	....
Free fatty acids	1.60	....
Neutralization value	....	193.0
Unsaponifiable matter, %	1.3	....
Maumené test (Archbutt's method)	98°	....
Liquid fatty acids, % (Muter's method)	....	87.0
Iodine value of liquid fatty acids	....	184.0

Cedar nut oil is used in Siberia as an edible oil, and is said to be technically of value as a fairly rapid drying oil of pale colour. Von Schmoelling states, however, that the "varnish" produced by heating the oil with 5% of manganese borate for 4 hours to 140° or 150° took twice as long to dry on glass as linseed oil varnish similarly prepared, and the product was very viscid and resembled a blown oil. The last-mentioned characteristic, together with the high price of the oil would, he thinks, prevent it from being used in the manufacture of varnish.

HEMPSEED OIL.

(See also p. 70.) This oil is obtained from the seeds of the hemp plant, *Cannabis sativa*. The expressed oil is at first greenish- or brownish-yellow, deepening in colour on exposure to the air. It consists of the esters of liquid and solid fatty acids, the former composed approximately, according to Hazura and Grüssner, of 70% of linolic, 15% of linolenic and isolinolenic and 15% of oleic acids; the solid fatty acids are said to be palmitic and oleic.

Hempseed oil has a high iodine value and is a strongly drying oil, though it dries less rapidly than linseed oil. It is used for making paints and varnishes, and as an adulterant of linseed oil; also for making soft soaps.

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[1] *Chem. Zeit.*, 1900, 24, 815.

		Observer
Maumené test	95°–96°	De Negris and Fabris.
Titer test of mixed fatty acids	15.6°–16.6°	Lewkowitsch.

LALLEMANTIA OIL.

(For constants see p. 70.) This oil, used in Russia as a lamp oil, is expressed from the seeds of *Lallemantia iberica.* It has excellent drying properties, and is not improbably used as a substitute for linseed oil.

LINSEED OIL.

(See special article, p. 323.)

NIGER SEED OIL. NIGER OIL.

(For constants see p. 70.) The seeds of *Guizotia oleifera*, which grows wild on the Gold Coast of Africa and is cultivated in Abyssinia and many parts of India, yield this oil, some being expressed in England. It is a good drying oil, of yellow colour, sometimes used as a substitute for linseed oil. It is said to have been used as a substitute for sesame oil and castor oil, though it would be easily distinguished from these oils. It has been employed as an adulterant of rape oil. Niger seed oil is said to contain but little stearic or palmitic acid, and hence soap made from it, though very white, is soft. A sample tested by the reviser gave a temperature-rise of 100° in Maumené's test. The viscosity of the oil is about two-thirds that of rape oil at 60° to 70° F.

PINE NUT OIL. FIRSEED OIL.

(For constants see p. 70.) Under this name are included the products of the nuts or seeds of different kinds of pine trees, such as *Pinus sylvestris*, *P. abies*, *P. picea*, etc. All have more or less pronounced drying characteristics and are used in the manufacture of paint and varnish. They probably differ a good deal from one another in chemical composition and properties.

POPPYSEED OIL. POPPY OIL.

(For constants see p. 70.) This oil is expressed from the seeds of the opium poppy, *Papaver somniferum*, the yield ranging from about 41 to about 50%, according to the variety. The seed is black, brown, yellow, or white, the latter being considered the richest. The plant is extensively cultivated in Egypt, Asia Minor, Persia, India, and China; it is also grown in France and Germany.

The cold-drawn oil extracted by the first pressing (*huile blanche*) is straw yellow in colour, limpid, and almost odourless; it has a pleasant almond-like flavour, and being slow to become rancid is largely used on the continent of Europe as a salad oil and also as an adulterant of olive oil. Owing to its drying properties and pale colour, which it retains, it is in demand for the manufacture of artists' pigments, the sun-bleached oil being used for white pigments and the unbleached but pale coloured oil for coloured pigments.[1] The inferior varieties of poppy oil, obtained by a second pressing (*huile rouge*) and from inferior seed, are used for soap-making and burning.

In a sample of oil from genuine poppy-seed, Tolman and Munson found 6.67% of solid fatty acids. The liquid fatty acids were found by Hazura and Grüssner[2] to consist, approximately, of oleic acid 30%, linolic acid 65%, linolenic and isolinolenic acid 5%. The calculated iodine value of such a mixture is 158, which approximates to the actual iodine value of the liquid fatty acids, found by Tortelli and Ruggeri to be 149.6 and by Tolman and Munson, 151.7. Hehner and Mitchell obtained no insoluble brominated glyceride from 4 samples of poppyseed oil.

Utz[3] has stated that practically all the commercial poppy oils examined by him contained more or less (up to 40%) of sesame oil, not added as an adulterant, sesame seed and oil being dearer than those of the poppy, but due to careless methods of manufacture, the two kinds of oil being expressed in the same works. The sesame oil is detected by its lower iodine value, and by the colour tests of Soltsein and Baudouin. Owing to this admixture, Utz believes the iodine value of genuine poppyseed oil, usually stated as 130 to 141, has been generally understated. The oil which he extracted by petroleum ether from three varieties of seed gave the following results:

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[1] Lotter, *Chem. Zeit.*, 1894, **18**, 1696.
[2] *Monatsh. Chem.*, 1888, **9**, 180.
[3] *Chem. Zeit.*, 1903, **27**, 1176.

Oil from	Iodine value	Butyro-refractometer at 15°
Indian poppyseed	153.48	78.1
Levantine poppyseed	157.52	78.4
German poppyseed	156.94	78.4

A specimen of commercial poppy oil which probably contained less than 5% of sesame oil had an iodine value of 151.65, and another, which gave only faint indications of sesame oil by the colour tests, absorbed 150.63% of iodine. It may be mentioned, however, that Tolman and Munson obtained iodine values of 133.2 and 134.9 from cold-drawn poppy oil expressed from seed which they state was identified as that of *P. somnifera*.

Utz confirms Bishop's statement that pure poppy oil is inactive, and suggests that the sample examined by Crossley and Le Sueur which had a rotation of +4′ may have contained sesame oil.

The viscosity of poppyseed oil at 70° F. is about two-thirds that of refined rape oil at the same temperature. 4 samples tested by Crossley and Le Sueur required from 254 to 259 seconds for the outflow of 50 c.c. from Redwood's viscometer, water at 70° F. requiring 25.4 seconds from the same instrument.

Other results for poppy oil are:

		Observer
Maumené test	86°–88°	Archbutt.
Sp. gr. of mixed fatty acids at 100°/100°	0.8886	Archbutt.
Titer test of mixed fatty acids	15.4°–16.2°	Lewkowitsch.

SAFFLOWER OIL.

(For constants see p. 70.) Safflower or saffron oil is the product of the seeds of the safflower (saffron) plant, *Carthamus tinctorius*, which is being increasingly cultivated in the Caucasus and in Turkestan;[1] it was at one time extensively cultivated all over India, and is still grown to some extent in that country. The oil is obtained by expression or extraction, the yield being about 20%. It has a pleasant taste, especially when obtained from the husked seeds, when it is of better quality than that obtained from the unhusked seeds. It has a bright yellow colour, and a taste very similar to that of sunflower oil. It is a good drying oil. The viscosity of the samples examined by Crossley and Le Sueur[1] was about two-thirds that of refined rape oil, 50 c.c. requiring from 243 to 294 seconds to flow from Redwood's viscometer at 70° F. The same observers obtained butyro-refractometer readings at 40° from 65.2 to 68.2.

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[1] Tylaikow. *J. Soc. Chem. Ind.*, 1902, **21**, 864.

According to Le Sueur,[2] the insoluble fatty acids of safflower oil consist of about 10% of solid acids (palmitic and stearic) and 90% of liquid fatty acids (oleic and linolic). No linolenic acid is present.

SUNFLOWER OIL.

(For constants see p. 70.) This oil is expressed from the seeds of the sunflower, *Helianthus annuus*, which is widely grown in southern Russia. The cold-pressed oil is pale yellow and of pleasant, mild taste and odour. It is used for culinary purposes, also as the vegetable oil in margarine, and has been detected as an adulterant of olive oil. Oil of the second pressing, which is more coloured, is used as a lamp oil, and in the manufacture of varnishes as a substitute for linseed oil, but it dries much more slowly than the latter. It is also used for soap-making.

Sunflower oil contains the glycerides of palmitic, oleic, and linolic acids, and probably also of linolenic and isolinolenic acids in small proportion. Tolman and Munson obtained 3.67 and 4.10%, respectively, of solid fatty acids from 2 samples, which also gave the following results: iodine values, 108.3 and 104.1; iodine values of the liquid fatty acids, 117.8 and 113.8. Tortelli and Ruggeri found the iodine value of the liquid fatty acids 154.3, from a sample of oil which absorbed 137% of iodine. A sample examined by Jean[3] contained 0.72% of unsaponifiable matter.

TUNG OIL. CHINESE WOOD OIL. JAPANESE WOOD OIL. WOOD OIL.[4]

(For constants see p. 70.) Tung oil is derived from the seeds of *Aleurites cordata* (*Elæococca vernicia*) a plant which is grown extensively in both China and Japan, also of *A. fordii*[1] and perhaps other species of *Aleurites*. The seeds contain 53% of oil, of which about 40% is obtained by expression.

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[1] *J. Soc. Chem. Ind.*, 1898, 17, 932.

[2] *J. Soc. Chem. Ind.*, 1900, 19, 104.

[3] *Ann. Chim. Anal.*, 1901, 6, 166.

[4] The term "wood oil" is also applied to Gurjun balsam, an oleoresin obtained from the East Indies.

Tung oil is either golden-yellow or dark brown in colour, according to whether it has been expressed in the cold or with the aid of heat, and it has, or develops on keeping, a somewhat pungent, peculiar odour, suggestive of bacon fat. It is the most powerful drying oil known, and is used extensively in China, the darker kind for caulking and varnishing junks, shop fronts, etc., and making putty, and the better sort for varnishing furniture. The light coloured oil of late years has been imported into Europe and America, chiefly from China, and used in the manufacture of lacquers and varnishes, though owing to the peculiar manner in which the oil dries, forming a film which is not transparent and elastic like that formed by linseed oil, but opaque and waxy looking, crumbling when rubbed, and to its property of gelatinising when heated to 250°, special treatment is necessary in using it.

Tung oil is composed of the esters of fatty acids, 25% of which were found by Cloëz to consist of ordinary oleic acid and 75% of an acid to which he attributed the formula $C_{17}H_{30}O_2$ and named *eloemargaric acid*, but which has been shown by Kametaka[2] to be a stereoisomeride of linolic acid, having the formula $C_{18}H_{32}O_2$. Walker and Warburton obtained little or no (0.39% to nil) insoluble brominated glyceride by adding bromine to a solution of tung oil in ether and acetic acid. From 2 samples, Jenkins obtained 10.4 and 10.6%, respectively, of glycerol.

Tung oil possesses the remarkable property of becoming *polymerised by heating*, a fact first observed by Cloëz. Jenkins[3] found that by heating the oil to 250° for 2 hours in a closed flask, out of contact with the air, it became converted into a sticky elastic jelly. Another sample formed a hard, dry, elastic solid when similarly treated. In an investigation of polymerised tung oil, Normann[4] found the saponification value of the polymerised oil only slightly lower than that of the original oil (190.5 compared with 195.5), while the neutralisation value of the liberated fatty acids was even less changed. The iodine value of the fatty acids, however, was found to be 101.3 as compared with 162.4, and the molecular weight in benzene solution ascertained by the freezing-point method showed that while the fatty acids of the original oil have a molecular weight of 399.6 to 432.8, those of the polymerised oil gave values ranging from 554.4 to 699.6. In a further experiment, in which the oil was heated for several hours in a sealed tube at 300 to 320°, the iodine value of the fatty acids was reduced to 68.5 and the molecular weight increased to 852.0, showing that in this case polymerisation had proceeded still further. Polymerised tung oil is insoluble in the usual solvents, and hence the molecular weight of the polymerized oil itself could not be determined.

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[1] *Bull. Imp. Inst.*, 1907, **5**, 134.
[2] *J. Chem. Soc. Trans.*, 1903, **83**, 1042.
[3] *Analyst*, 1898, **23**, 113.
[4] *Chem Zeit.*, 1907, **31**, 188.

Iodine also has a remarkable action on this oil. Jenkins found that if a saturated solution of iodine in chloroform or carbon disulphide be dropped upon the oil it immediately solidifies it. Bromine has no such action. If 1 grm. of tung oil be dissolved in 5 c.c. of chloroform, mixed with 5 c.c. of a saturated solution of iodine in chloroform and stirred, the whole may become suddenly converted into a jelly in a few seconds. Some samples take much longer, and may need gentle warming; some refuse to gelatinise unless a larger quantity (2 to 4 grm.) of the oil be taken.

Tung oil *dries very rapidly*. 0.5 grm. was exposed to the air in a water-oven at about 100° on a watch glass. In about 3 minutes a dry ring formed round the spot of oil, and in 3 hours the oil was dry throughout and had gained 1.56% in weight. Raw linseed oil similarly treated had just begun to dry at the edges in 3 hours, and had gained 0.92% in weight (Archbutt).

5 grm. of tung oil stirred in the cold with 2 c.c. of carbon disulphide and 2 c.c. of sulphur chloride for 90 seconds suddenly stiffened to a thick and sticky jelly, not nearly so hard as the product obtained in a similar manner from either castor or linseed oil.[1]

In the *elaidin test*, Jenkins obtained a brownish-red product, consisting of an oily layer resting on a nearly solid portion. When stirred up, the whole would scarcely flow.

In the *Valenta test*, using glacial acetic acid, Jenkins found the turbidity temperatures of two samples to be 44° and 47°, respectively.

Strong sulphuric acid immediately solidifies tung oil, forming a black clot, but by mixing 10 grm. of the oil with 40 grm. of olive oil, Jenkins found it possible to measure the rise of temperature, and after making a correction for the heat developed by the olive oil obtained

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[1] Jenkins. *J. Soc. Chem. Ind.*, 1897, 16, 195.

specific temperature reactions of 298 and 330 with two different samples.

Nitric acid (1.4) rapidly converts tung oil into a tough mass, which darkens and becomes more brittle on standing.

The *viscosity* seems to be very variable, possibly due to a partial polymerisation of some samples. Two samples tested by Jenkins required, respectively, 1433 and 858 seconds for the outflow of 50 c.c. from Redwood's viscometer at 60° F.

Halphen's reaction for cottonseed oil gives no colouration with genuine samples of tung oil.

Commercial samples of tung oil have been found to contain from 0.44 to 0.74% of *unsaponifiable matter* and from 0.39 to 5.30% of *free (oleic) acid.*

The *mixed fatty acids* have been found to solidify at 31.2 to 37.2° and to have an iodine value of 150 to 159.

Tung oil is said to cause severe ulcers when brought into contact with the skin,[1] and its use in cosmetic and similar preparations (for which patents have been taken out) should be prohibited.

Blakeman[2] has patented as a drying oil a mixture of 85 parts of a "non-drying oil such as cottonseed oil" and 15 parts of tung oil mixed with a drier.

WALNUT OIL. NUT OIL.

(For constants see p. 70.) This oil is obtained by expression from the kernels of the walnut, *Juglans regia,* which, if the nuts have been kept for 2 to 3 months after they have been gathered, yield from 63 to 66%; if kept too long, the oil expressed from the kernels may be rancid.

The first-expressed, "virgin," oil is almost colourless, with faint odour and not unpleasant flavour; it is largely used in some parts of Europe as a substitute for olive oil for edible purposes. The second-pressed or "fire-drawn" oil is greenish-coloured, with an acrid flavour. Being an excellent drying oil, forming a varnish which is pale in colour and less liable to crack than linseed oil varnish, walnut oil is much used for preparing artists' colours. It is also a good lamp oil, and can be used for making soft soap.

Walnut oil contains the esters of myristic, lauric, oleic, linolic, linolenic and isolinolenic acids. According to Hazura and Grüssner,

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[1] Hertkorn. *Chem. Zeit.*, 1903, 27, 635.

[2] U. S. Patent, 767682, 1904.

80% of the liquid fatty acids consist of linolic acid, 13% of linolenic and isolinolenic acids, and 7% of oleic acid. The calculated iodine value of this mixture of liquid acids is 187 (Hehner and Mitchell); the iodine value of the liquid fatty acids determined by Tortelli and Ruggeri was found to be 166.8, the oil from which they were obtained having an iodine value of 148.9.

5 samples of cold-pressed Bulgarian walnut oil examined by Petkow[1] gave results as follows:

Sp. gr. at 15°	0.9255–0.9260
Refractometer reading, 40°	67–68
Iodine value	147.92–148.43

A sample from the Punjab examined by Crossley and Le Sueur gave a butyro-refractometer reading of 64.8 at 40°, and 50 c.c. required 232 seconds to flow from Redwood's viscometer at 70° F.

A sample of black-walnut oil from *J. nigra* examined by Kebler[2] was a straw yellow coloured oil, having an agreeable walnut-like odour and taste, and gave the following results:

Sp. gr. at 15°	0.9215
The oil became turbid at	−12°
Acid value	8.6–9.0
Saponification value	190.1–191.5
Iodine value	141.4–142.7
Hehner value	93.77
Reichert-Meissl value	15 c.c.
M. p. of fatty acids	0°

Confirmation of the high Reichert-Meissl value of this sample is required, seeing that ordinary walnut oil has no Reichert-Meissl value.

Walnut oil is liable to adulteration with other oils, most of which would lower the iodine value. Poppy oil would not appreciably alter the ordinary constants, and Bellier[3] has proposed a test for this oil based upon the difference in solubility of the solid fatty acids in 70% alcohol at 17° to 19° in presence of a definite amount of potassium acetate. 1 c.c. of the oil is warmed in a test-tube with 5 c.c. of a solution of 16 grm. potassium hydroxide in 100 c.c. of 91 to 93% alcohol, until a clear solution is obtained, a similar test being simultaneously made with a walnut oil of known purity. The tubes are then closed and kept at about 70° for 30 minutes. A quantity of dilute acetic acid (1 volume of glacial acetic acid and 3 volumes of water) exactly equivalent to the potassium hydroxide is added, and the tubes and contents are cooled, first to 25°, and then to 17° to 19° with frequent shaking. Under these conditions, pure walnut oil requires a much longer time to give even a small precipitate of fatty acids than an impure sample, while poppy oil speedily gives an abundant precipitate, and other oils also give a precipitate more quickly and in larger quantity than walnut oil. The test is said to be capable of detecting 10% of poppy oil, and has been confirmed by Balavoine.[1]

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[1] *Zeit. Nahr. Genussm.*, 1901, **4**, 828.
[2] *J. Frank. Inst.*, 1901, **151**, 394.
[3] *Ann. Chim. Anal.*, 1905, **10**, 52.

The difference in the yields of brominated glycerides insoluble in ether-acetic acid affords a means of detecting adulteration of walnut oil with oils which are not readily detected by other tests. From genuine walnut oil, Hehner and Mitchell obtained a yield of 1.5 to 1.9%; from poppy oil, none; and from linseed oil, 24 to 26%.

V. CASTOR OIL GROUP.

Castor Oil.	**Curcas Oil.**
Croton Oil.	**Grape-seed Oil.**

CASTOR OIL.

(See also p. 71.) Castor oil is expressed from the seeds of *Ricinus communis*, of which it constitutes nearly half the weight. It is also prepared by extraction. Cold-pressed ("cold-drawn") oil of the first quality is used as a medicinal purgative, but the lower grades are largely employed for lubrication by the Indian and Cape railways, for the manufacture of Turkey-red oils, for soap-making and leather dressing. It does not readily dry on exposure to the air, nor does it easily turn rancid (Lewkowitsch).

Castor oil is a transparent, colourless, or pale greenish-yellow liquid, having a faint odour and disagreeable taste. At a low temperature it thickens and deposits white granules, and at or about —18° it solidifies to a yellowish mass.

Castor oil is distinguished in its physical characters from most other fixed oils by its high sp. gr. and viscosity, ready solubility in alcohol and insolubility in petroleum spirit. These characters are of value for the assay of commercial samples, and are described below. Castor oil is dextrorotatory. 23 samples of Indian castor oil examined by Deering and Redwood[2] in a Hofmann-Laurent polarimeter with 200 mm. tube, caused a rotation ranging from +7.6° to +9.7°. Dowzard[1] gives +8° to +9°; Rakusin[2] +8° to +8.65°. Lythgoe[3] found the optical rotation of 44 samples of genuine castor oil to range from +23.4° to +26.1° (Ventzke, 200 mm., 20°); these numbers fall within the limits given by Deering and Redwood, whose values correspond with 21.9° to 28° Ventzke.

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[1] *J. Soc. Chem. Ind.*, 1906, **25**, 499.
[2] *J. Soc. Chem. Ind.*, 1894, **13**, 959.

Castor oil consists mainly of triricinolein, the glyceride of two isomeric hydroxylated acids, ricinoleic and isoricinoleic. Small quantities of tristearin and of the glyceride of dihydroxystearic acid are also present. Palmitin and olein are absent. Lewkowitsch[4] points out that less saturated fatty acids than ricinoleic must also be present, otherwise the iodine value of castor oil would not exceed about 67.

Crude Ricinoleic Acid, $HC_{18}H_{33}O_3$, may be prepared from castor oil by the method employed for the preparation of oleic acid from oils; or castor oil may be saponified, and the soap fractionally precipitated with calcium chloride. The first third should be rejected. The later fractions are purified by crystallisation from alcohol, and decomposed by dilute hydrochloric acid.

Ricinoleic acid is a thick oily liquid, which solidifies below 0°. It is insoluble in water, but is miscible in all proportions with alcohol and ether. The alcoholic solution has an acid reaction, an unpleasant, persistent, acrid taste, and does not oxidise in the air. Like oleic acid, it combines with the atoms of bromine, and by treatment with nitrous acid is gradually converted into a stereo-isomer, ricinelaïdic acid, a body crystallising from alcohol in white needles, melting at 50°, and forming an additive compound with Br_2. When heated with phosphorus, iodine, and water, ricinoleic acid yields an iodo-acid, which by the action of nascent hydrogen (hydrochloric acid and zinc) is converted into stearic acid.

When distilled in a partial vacuum, ricinoleic acid yields enanthal or normal heptoic aldehyde, $C_6H_{13}.CHO$, and an acid of the acrylic series. This behaviour may be used for the detection of castor oil. For this purpose the sample should be saponified, and the fatty acids liberated and rapidly distilled in a small retort. The distillate is shaken with a saturated solution of acid sodium sulphite, the resultant crystals pressed, dissolved in a solution of sodium carbonate, and the liquid distilled in a current of steam. The enanthal will collect on the surface of the distillate as a highly refractive liquid, of peculiar aromatic odour, boiling at 154°. Enanthal is also produced by subjecting the alkali-metal salts of ricinoleic acid to dry distillation, but if sodium hydroxide be present in addition, sodium sebacate is formed, and methyl-hexyl carbinol and methyl-hexyl ketone are found in the distillate.

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[1] *Chemist and Druggist*, 1901, **58**, 325.
[2] *Chem. Zeit.*, 1906, **30**, 143.
[3] *J. Amer. Chem. Soc.*, 1905, **27**, 888.
[4] Oils, Fats and Waxes, II, 326.

Ricinoleic acid forms a series of salts, many of which are soluble in, and may be crystallised from, alcohol or ether.

The oleo-refractometer value of castor oil is given in the table on p. 44. The butyro-refractometer readings of the 44 samples examined by Lythgoe averaged 81.2 at 20°, and 78.1 at 25°, the variations from these numbers being slight and not exceeding ±0.5. Lythgoe gives the values for each 0.5° from 15° to 35°.

The following are some results of examination of the mixed fatty acids of castor oil (see also p. 71):

		Observer
Sp. gr. at 15.5°	0.9509	Allen.
Sp. gr. at 98°–99°	0.8960	Allen.
Solidifying-point	3°	Hübl.
Refractive index at 60°	1.4546	Thoerner.
Iodine value of mixed fatty acids	87–88	
Iodine value of liquid fatty acids	106.9	Tortelli and Ruggeri.

COMMERCIAL CASTOR OIL.

The peculiar physical characters of pure castor oil distinguish it sharply from most other oils, but it is liable to adulteration with oils, such as cottonseed or rape oils, blown oils, rosin oil, etc., which may be lower in price, for the detection of which the following tests may be used.

The *sp. gr.* of genuine castor oil is exceptionally high, and should lie between 0.959 and 0.968 at 15.5°. Adulteration with any other natural fixed oil or mixture of oils would lower the sp. gr., and although this might be adjusted by the addition of rosin oil, which often has a sp. gr. as high as 0.998, the presence of the latter would be easily detected by an estimation of the *unsaponifiable matter*, which in genuine castor oil is usually less than 0.7%. Blown rape or cottonseed oil might be added without altering the sp. gr., and without causing any large increase of the unsaponifiable matter, but these oils would be detected by some of the following tests.

The *viscosity* of castor oil at the ordinary temperature exceeds that of all other natural fixed oils, but is approached by that of rosin oil and may be exceeded by that of blown oil. Twenty-three samples of Indian castor oil tested by Deering and Redwood in the Redwood viscometer required from 1160 to 1190 seconds for the outflow of 50 c.c. at 100° F. The absolute viscosity, determined by Archbutt and Deeley, was found to be 2.729 at 100° F., 0.605 at 150° F., and 0.169 at 212° F.[1]

The *solubility in alcohol* of castor oil is greater than that of any oil likely to be used as an adulterant. Absolute alcohol dissolves castor oil in every proportion; 90% alcohol (sp. gr. 0.834) dissolves less, 1 volume of castor oil requiring from 2.4 to 2.94 volumes of 90% alcohol at 20° according to experiments by Itallie,[2] or from 3 to 4 volumes according to Dowzard.[3] A genuine sample tested by Archbutt dissolved perfectly in 2 volumes of 90% alcohol at 15°. 23 samples of Indian castor oils examined by Deering and Redwood were completely soluble in 3 volumes of alcohol of sp. gr. 0.830 at 15.5°. From these results it appears that castor oil, if genuine, should dissolve completely in 3 volumes of 90% alcohol at 20°. It is usual, however, to employ 5 volumes of alcohol, as recommended in the British Pharmacopœia. Archbutt and Deeley[4] found that when only 5% of either rape, blown rape, cotton seed, poppy, maize, or curcas oils were mixed with castor oil, 5 volumes of 90% alcohol gave a strongly turbid mixture at 15°, which deposited a small quantity of oil on standing. The following test, originally recommended by Finkener[5] (who used a slightly stronger alcohol), may therefore be employed with confidence as a rapid method of assay: Measure exactly 10 c.c. of castor oil in a graduated, stoppered test cylinder, add 50 c.c. of alcohol (sp. gr. 0.834) and well mix. If genuine, a clear and bright solution will be obtained at 15°. If as little as 5% of foreign oil be present, the liquid will remain strongly turbid, even on warming to 20°. *Oleic acid* would not be detected by the alcohol test, but it can be estimated with accuracy by titrating the sample with standard alkali, the acidity of genuine commercial castor oil being usually under 3%.

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[1] Lubrication and Lubricants, p. 167.

[2] Lewkowitsch, Oils, Fats and Waxes, II, 330.

[3] *J. Soc. Chem. Ind.*, 1901, **20**, 370.

[4] Lubrication and Lubricants, p. 319.

[5] *J. Soc. Chem. Ind.*, 1887, **6**, 148.

Castor oil is readily soluble in *glacial acetic acid.* It is easily miscible with an equal measure of that solvent at the ordinary temperature, whereas most other fixed oils, except croton oil, are only dissolved on heating, and yield solutions which become turbid before they have again cooled to the ordinary temperature.

The behaviour of castor oil with *petroleum spirit* is highly characteristic. As far as has been recorded, all other fixed oils dissolve with facility in petroleum spirit, and are probably miscible in all proportions therewith, and with mineral lubricating oil. On the other hand, castor oil is not soluble in petroleum spirit, though it is itself capable of dissolving its own volume of that liquid. The following information is given on the authority of Archbutt and Deeley:[1] At 15° castor oil is practically insoluble in petroleum spirit and in burning oil. In "865" Scotch shale oil, at the same temperature, it dissolves to the extent of about 1 to 1.5%; "890" shale oil dissolves about 2 to 2.5% of it; and "907/12" American mineral oil dissolves rather more. Therefore, at the ordinary temperature, castor oil is very sparingly soluble in mineral oils; the solubility is greater the more dense and viscous the mineral oil; it increases with rise of temperature and diminishes as the temperature falls.

On the other hand, castor oil is able to dissolve mineral spirit and mineral oils in proportions which decrease as the sp. gr. of the mineral oil increases. The following table shows the maximum volumes which were found to give a clear solution at 15° with 10 c.c. of pure castor oil,

Mineral oil used	Sp. gr. at 15.5°	Maximum volume miscible with 10 c.c. of pure castor oil at 15°
Mineral (petroleum) spirit	0.692	9.2 c.c.
"White Rose" petroleum	0.788	5.5 c.c.
Scotch shale oil	0.865	3.7 c.c.
Scotch shale oil	0.890	2.45 c.c.
American pale mineral oil	0.907–0.912	1.7 c.c.

Although pure castor oil almost refuses to mix with mineral lubricating oil, the difficulty entirely disappears if a third oil, such as rape, tallow, or lard oil, is present, a clear mixture of the three being readily obtained. Pure castor oil mixes with refined rosin oil in all proportions.

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[1] Lubrication and Lubricants, p. 114.

The *acetyl value* (see p. 32) of castor oil (146.7 to 150.5) exceeds that of any other known oil, and is one of the most valuable indications of its purity. Although blown oils also have high acetyl values (about 45 to 65) they do not nearly approach castor oil in this respect, and the detection of 10% of blown oil in castor oil is possible. Grape seed oil, if added to castor oil, would lower the sp. gr.

The *Hehner value* (95.3 to 95.5%) and the *iodine value* would be lowered by adulteration with blown oil; the *Reichert-Meissl value*, *Maumené thermal value*, and *saponification value* would, on the other hand, be raised. Refined *rosin oil*, which has been extensively employed for the adulteration of castor oil, neutralises no alkali, or only a trifling quantity, and would, therefore, lower the saponification value.

The high *optical rotation* caused by castor oil has already been referred to and would be lowered by most other natural fixed oils, except croton oil and laurel oil (Rakusin). It would not be available in the presence of *rosin oil*, which is strongly dextrorotatory. Some samples of sesame oil have a marked rotatory power (see p. 142). The *refractometer* would also be useful. Lythgoe mentions an instance in which 50% of *cottonseed oil* was found in a sample of "castor oil" from Massachusetts. This was detected at first by the low optical activity of the sample, and was confirmed by the low refractive power and sp. gr. and the high iodine value, also by Halphen's colour reaction.

Among other possible adulterants, *poppyseed oil* would lower the sp. gr., acetyl value, and viscosity, and would raise the iodine value; *lard oil* would lower the oleo-refractometer value, sp. gr., viscosity, acetyl, and iodine values; *coconut oil* would raise the saponification value and would lower the sp. gr., Hehner value and iodine value; and *seal oil* would lower the sp. gr., viscosity and acetyl value, and would raise the iodine value. *Sesame oil* would be detected by the characteristic colour tests for this oil.

The formation of sebacic acid, when the sample is distilled alone or with a quantity of alkali insufficient for its complete saponification, may be employed as a test for foreign fixed oils in castor oil.

When castor oil is distilled at 300° until it has lost from 5 to 10% of its weight, a yellowish-brown oil with green fluorescence remains, which is miscible in all proportions with mineral oils, ceresin or vaseline, and is not soluble in alcohol or acetic acid. The name "floricin" has been given to this product. According to Fendler,[1] it contains the ester of undecylenic acid. A similar product is obtained by heating the oil in an autoclave to 260°–300° under a pressure of 4 to 6 atmospheres for about 10 hours.[2]

Estimation of Castor Oil.—Lane,[3] having found that lead ricinoleate is insoluble in petroleum ether, has devised the following method of estimating castor oil in mixtures, soaps, and alizarin oils. The liquid acids in these cannot be estimated by the lead-soap and ethylic ether method, because lead stearate and palmitate are soluble in a solution of lead rincinoleate in ethylic ether.

From 3 to 3.5 grm. of the oil or fatty acids are taken. If the sample be sulphonated (Turkey-red oil), a quantity sufficient to yield this amount of fatty acid must be first boiled for about 2 hours with dilute hydrochloric acid (1 : 5), with frequent shaking, until desulphonation is complete, the acid liquid being then poured into a separating funnel, shaken with ether, and the ethereal solution washed with water until free from acid. The ether having been distilled off, the fatty matter is weighed and saponified with alcoholic potassium hydroxide, a drop of phenolphthaleïn added, the solution rendered slightly acid with acetic acid and then very faintly pink with N/10 sodium hydroxide. The liquid is then slowly poured into a boiling mixture of 200 c.c. of water and 30 c.c. of a 10% solution of lead acetate contained in a 500 c.c. Erlenmeyer flask, the boiling is kept up for 5 or 6 minutes, and the liquid is then cooled by rotating the flask under a stream of running water, the movement being continued until the lead soaps adhere to the sides of the flask and the aqueous solution is clear. If it remain milky, desulphonation was not complete, and the test must be repeated. The aqueous solution is poured off, or filtered if necessary, the flask is then heated on the steam-bath until the contents are melted, again cooled, and any remaining water shaken out.

The flask containing the dry lead salts is heated, and about 10 c.c. of petroleum spirit are added, which usually mixes with the soaps and renders them more fluid. 75 to 80 c.c. more petroleum spirit are added, and the solution is boiled under a reflux condenser. It is then poured into a stoppered, graduated, 500 c.c. cylinder of thin glass, having a stop-cock just below the 250 c.c. mark, or into a 500 c.c. graduated flask. The flask containing the salts is repeatedly rinsed with petroleum ether, boiling each time, and transferring as much as possible of the lead soaps to the cylinder or flask, using about 200 to 225 c.c. of petroleum spirit altogether. The ethereal solution is then diluted nearly to the 500 c.c. mark with petroleum spirit boiling at 28° to 30°, the whole is boiled for 1 minute (neglect of this detail will cause an inaccurate result) and allowed to stand in a cool place for at least 3 hours, and preferably all night, in order that the lead ricinoleate, etc., may completely separate.

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[1] *Deutsch. pharm. Ges. Ber.*, 1904, **14**, 135.
[2] *Eng. Pat.* 24935, 1905.
[3] *J. Soc. Chem. Ind.*, 1907, **26**, 597.

If the sample contains 80% or more of castor oil, petroleum spirit of 38° to 40° b. p. is used for rinsing and washing the flask; if under 80%, that of 28° to 30° b. p. is used, the percentage of castor oil present being judged, approximately, by the fact that when under 80% the soaps will dissolve in the hot spirit of 30° b. p., while if over 80% a semi-fluid mass remains which is more perfectly extracted by the solvent of higher b. p. It is essential, however, that the greater part of the spirit used for the dilution should be of the lower b. p. The lead ricinoleate is precipitated from this, on cooling, as a characteristic, flocculent mass resembling aluminum hydroxide, lead stearate and palmitate forming white, slowly subsiding powders.

After the complete separation of the insoluble lead salts, the liquid is diluted to exactly 500 c.c., shaken and allowed to settle. 250 c.c. are then drawn off, filtered if necessary, distilled down to 75 or 80 c.c., shaken in a separating funnel with 10 c.c. of 10% acetic acid, and washed with water until the washings are perfectly neutral to phenolphthaleïn and made alkaline by one drop of N/10 sodium hydroxide. The solution is then distilled from a 200 c.c. Erlenmeyer flask until most of the petroleum spirit has been expelled, mixed with 50 c.c. of neutral alcohol, and titrated with N/10 sodium hydroxide. The volume of decinormal alkali used $\times 0.0282$, gives the equivalent weight of oleic acid, and if we assume that the other oils in the mixture are vegetable oils, such as olive, maize, etc., which contain approximately 80% of liquid acids, the result $\times \frac{100}{80}$ represents oil other than castor oil. If the admixed oil can be identified, however, its percentage of liquid acids should, of course, be substituted for 80. The weight thus obtained, multiplied by 2, subtracted from the weight of oil or mixed fatty acids taken, multiplied by 100 and divided by the weight taken, gives the percentage of castor oil in the sample. If the mixed fatty acids are used for the estimation, the result must of course be divided by 0.95 to give the equivalent of neutral oil.

Lane obtained the following results by this method:

Mixture prepared		Castor oil found, %
Castor oil	Olive oil	
50	50	47.83
70	30	69.96
85	15	84.57
85	15	84.45

A commercial sample, composed of castor oil, olive oil, and oleic acid, said to contain 75% of castor oil, was found to contain 76%.

ALIZARIN OIL. TURKEY-RED OIL.

In dyeing cotton goods red with alizarin, the employment of a fatty acid at one stage of the process is essential. Experience has shown that the best results are obtained by employing the ammonium salt of recinoleosulphuric acid, $C_{18}H_{33}(HSO_3)O_3$, a substance which is obtained, mixed with unaltered esters and with the products of its decomposition (see "Sulpholeic Acid"), by the action of sulphuric acid on castor oil. The details of the method of preparation vary considerably; a common plan is to treat castor oil with strong sulphuric acid, added slowly with stirring, so that the temperature does not rise above 35°. The excess of sulphuric acid is then removed by agitating the product with water and then with a solution of common salt or, preferably, sodium sulphate, and the oily layer of crude ricinoleosulphuric acid is partially neutralised with ammonia, or with a mixture of ammonia with potash or soda, and diluted to the required strength. The product, which is a complex mixture of ricinoleosulphuric, ricinoleic, and polyricinoleic acids, existing partially in the free state, partly combined with ammonia or soda, and partly as mixed glycerides, together with unaltered esters and water, constitutes "alizarin or Turkey-red oil," also called "sulphated oil," "soluble oil," "red oil" or "olein."[1] True Turkey-red oil is made from castor oil exclusively (Wilson), but similar products are prepared from olive oil and cottonseed oil; these latter may be distinguished as olive Turkey-red oil and cottonseed Turkey-red oil, respectively.

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[1] The composition and mode of action of Turkey-red oils have been the subject of numerous researches. See Lewkowitsch, Oils, Fats and Waxes, III, 154; Alder Wright and Mitchell, Oils, Fats and Waxes, p. 185; Knecht and Rawson, A Manual of Dyeing, p. 160.

When castor Turkey-red oil is shaken with water and ether, the sulphonated fatty acids are dissolved by the water and the non-sulphonated acids and unaltered glycerides by the ether; the former may be caused to separate from the aqueous portion by saturating it with common salt or sodium sulphate, and the latter can be recovered by evaporating off the ether. The solubility of Turkey-red oil in water is due to the presence of the sulphonated acid.

The proportion of fatty matter present in alizarin oil varies considerably. It may be as low as 40, and occasionally reaches 65%, the usual proportion being about 50%. The amount required should be specified by purchasers and controlled by analysis.

Turkey-red oil, if properly prepared from pure castor oil, when *largely* diluted, even with hard water, will bear the addition of ammonium hydroxide to alkaline reaction without showing any turbidity on standing for several hours. A turbidity or precipitate denotes the presence of solid fats, and indicates the employment of either impure castor oil (*e.g.*, castor oil foots) or of rape, cottonseed, olive, or other oil containing stearin or palmitin.

The sp. gr. of Turkey-red oil is very variable. According to Wilson,[1] the sp. gr. of a 45% oil ranges from 1.017 to 1.035.

The analysis of Turkey-red oil may have as its object the estimation of (1) the amount and nature of the fatty matter, alkali, etc., contained in the sample, and (2) the source of the fatty matter and the presence or absence of adulterants.

In the estimation of the *total fatty matter* it is customary to decompose the sulphonated oils by boiling with dilute hydrochloric acid. Lewkowitsch[2] recommends *Benedikt's* method. About 4 grm. of the sample are accurately weighed into a porcelain basin, and 20 c.c. of hot water are added gradually. Should the liquid be turbid, ammonia is run in until it is faintly alkaline to phenolphthaleïn. A clear solution will thus be obtained. 15 c.c. of dilute sulphuric acid (equal volumes of strong acid and water) are next added and an accurately weighed quantity, about 10 grm., of paraffin wax. The mixture is heated until a clear oily layer floats upon the surface. It is then made quite cold, the solidified cake is removed, carefully dried, and weighed. From the weight, that of the added paraffin wax is deducted, and the remainder represents the total fatty matter in the quantity taken.

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[1] *J. Soc. Chem. Ind.*, 1891, **10**, 26.
[2] Oils, Fats and Waxes, III, 158.

According to Herbig,[1] the simplest method is that of *Finsler-Breinl.* 30 grm. of the oil are weighed into a flask of 210 c.c. to 250 c.c. capacity, having a long narrow neck graduated in tenths of a c.c. 100 c.c. of water and 25 c.c. of sulphuric acid (62° B = 1.753 sp. gr.) are added and the mixture is heated until the oily layer which forms is perfectly transparent. A hot solution of sodium chloride or sulphate is then poured into the flask to bring the oily layer into the neck, and after standing half an hour the volume is read off. Each 1 c.c. = 3% of fatty matter, but as the average sp. gr. of the oil is 0.945 the result should be multiplied by this factor.

In a later paper[2] Herbig recommends the following method. 10 grm. of the oil are heated in a flask with 50 c.c. of water, until dissolved, and the solution is then mixed with 25 c.c. of dilute (1:5) hydrochloric acid and boiled for 3 to 5 minutes. When cold, the contents of the flask are transferred to a separating funnel with water and well shaken with about 200 c.c. of ether. The aqueous layer is drawn off, and the ethereal solution washed with three successive quantities of cold water. The greater part of the ether is distilled off, the residue transferred to a beaker and the rest of the ether allowed to evaporate spontaneously. The residual oil is heated for 1 or 2 minutes over a free flame until bubbles cease to appear, then dried for 30 minutes at 105° and weighed. The aqueous extract and washings, if mixed and heated to expel the dissolved ether, may be used for estimation of the fatty sulphuric acid and glycerol.

To estimate the *total free acid,* Wilson dissolves 5 to 7 grm. of the oil in alcohol or alcohol-ether and titrates with N/2 alcoholic potassium hydroxide, keeping the temperature low and stirring rapidly so as to avoid local excess of alkali, owing to the great tendency of the esters in all Turkey-red oils to undergo hydrolysis. The amount of free acid, calculated as ricinoleosulphuric acid, in a 45% oil may range from 22 to 30%. This method is intended for Turkey-red oils prepared with sodium hydroxide or potassium hydroxide, but good results may be obtained even in the case of ammonia Turkey-red oils. Obviously, the figure obtained gives no idea as to the percentage of total fatty acids actually present, owing to the great difference in the molecular equivalents of the different acids. If this information be desired, the percentage of neutral oil should be estimated and the fatty acids got by difference.

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[1] *J. Soc. Chem. Ind.*, 1902, **21**, 367; from *Chem. Rev. Fett-Harz -Ind.*, 1902, **9**, 5.

[2] *Chem. Rev. Fett-Harz-Ind.*, 1906, **13**, 187, 211 and 241; abs. in *J. Soc. Chem. Ind.*, 1906, **25**, 1009.

For the estimation of the *neutral oil*, Lewkowitsch[1] dissolves 30 grm. of the sample in 50 c.c. of water, adds 20 c.c. of ammonia and 30 c.c. of glycerin, and shakes twice with ether, using 100 c.c. each time. The ethereal solution is washed with water to remove traces of soap, run through a dry filter into a tared flask, the ether distilled off, and the residual oil dried at 100° and weighed.

Scheurer-Kestner,[2] after pointing out the different shades produced in dyeing and printing by the *sulphonated* and *non-sulphonated fatty acids*, respectively, proposed a method of roughly estimating these volumetrically by titration with standard ammonia solution, dependent upon the fact that litmus becomes blue when the sulphonated acids are neutralised, while phenolphthaleïn does not become reddened until the neutralisation of the whole of the fatty acids present is completed. In a particular sample he found the molecular weight of the mixed non-sulphonated acids 472 and that of the sulphonated acids 402. The following are the molecular weights of some of the pure acids which may be present:

Ricinoleic	298
Di-ricinoleic	578
Ricinoleosulphuric	378
Di-ricinoleosulphuric	658

Jouillard[3] says this method gives inaccurate results, especially as diricinoleosulphuric acid is almost invariably present. He advises an estimation of the *molecular weight* of the fatty acids soluble and insoluble in water, by *Raoult's method*, taking care, in separating these by shaking with water and ether as already described, that the whole of the water-soluble acids are extracted. Jouillard also recommends an estimation of the glycerol and sulphuric acid in the sulphonated oil.

For the estimation of *fatty-sulphuric acid*, Herbig (*loc. cit.*) boils 4 grm. of the oil with 30 c.c. of dilute hydrochloric acid (1:5) for 40 minutes, removes the oil by shaking with ether, and estimates the SO_3 in the aqueous liquid by precipitation with barium chloride. From the weight obtained should be deducted the amount of SO_3

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[1] Oils, Fats and Waxes, III, 159.

[2] *Compt. rend.*, **112**, 158 and 395.

[3] *Bull. Soc. Chim.*, 1891, **6**, 638.

existing as sodium or ammonium sulphate, which Lewkowitsch estimates by dissolving a weighed quantity of the sample in ether, shaking repeatedly with small quantities of saturated brine free from sulphate, and estimating the SO_3 in the brine washings.

The *total alkali* may be estimated by titration. Wilson takes 5 to 7 grm., dilutes with water to about 50 c.c., and titrates with semi-normal acid, using methyl orange as indicator. The result is calculated to ammonia or sodium hydroxide. If both are present, the oil should be dissolved in ether and well shaken with dilute sulphuric acid. The ammonia, sodium hydroxide (and potassium hydroxide) can then be estimated in the aqueous washings by the usual methods.

Traces of *iron* seriously affect the brilliancy of alizarin colours. If 10 c.c. of the oil is shaken in a stoppered cylinder with 20 c.c. of dilute sulphuric acid (1:1) and a few drops of potassium ferrocyanide solution, and after adding 50 c.c. of ether if the mixture be again well shaken, even a trace of iron gives a blue ring at the junction of the ethereal and aqueous liquids.[1]

For the purpose of ascertaining the source of the oil with which the sample of Turkey-red oil has been prepared and the *detection of adulterants*, Wilson[2] saponifies 100 grm. by boiling with alcoholic potassium hydroxide and obtains the mixed fatty acids in the usual way. He then ascertains the *acetyl value*, *sp. gr.*, *m. p.*, and *saponification value*. The acetyl value should be determined by Lewkowitsch's method (see p. 32) and should be 125 or over if pure castor oil has been used in the preparation of the sample. A lower value would show that other oils have been used. The following average results were obtained by Wilson with mixed fatty acids from Turkey-red oils made from castor, olive, and cottonseed oils, respectively:

	Castor oil acids	Olive oil acids	Cotton-seed oil acids
Westphal gravity at 98°	0.892	0.851	0.872
M. p. by capillary tube	....	40°	44°
Neutralisation value	180–184	173–176	171–175

The fatty acids from castor Turkey-red oil deposit no more than traces of fat at 15.5°, while those from olive and cotton oils solidify.

Adulteration of Turkey-red oil with *mineral or rosin oil* would be detected by an estimation of the unsaponifiable matter.

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[1] *Leipziger Färber u. Zeugdr., Zeit.*, 1901, 4, 14, 153.
[2] *J. Soc. Chem. Ind.*, 1892, 11, 495.

CROTON OIL.

(See also p. 71.) Croton oil is obtained by expression or extraction with alcohol from the seeds of *Croton Tiglium*, the yield being about 53 to 56%. It is a brownish-yellow to dark reddish-brown, viscid oil, with disagreeable odour and acrid burning taste (*British Pharmacopœia*), intensely purgative and vesicatory.

The lighter varieties darken very much with age. Croton oil differs from castor oil in being soluble in petroleum spirit. It has slight drying power and forms no elaidin with nitrous acid. It is composed of the glycerides of tiglic acid and other higher homologues of oleic acid, and of stearic, palmitic, myristic, lauric, caproic, butyric, and acetic acids. Oleic acid itself has not been identified in the oil. Dunstan and Boole[1] have shown that the vesicating constituent is a neutral, resinous substance of empirical formula $C_{13}H_{18}O_4$, which forms but a small proportion of the so-called "croton-oleic acid" from which it is obtained.

Croton oil is more strongly dextrorotatory than castor oil. Rakusin,[2] using a Soleil-Ventzke instrument with 200 mm. tube, obtained the following values:

Croton oil, +14.5° to +16.4°.
Castor oil, + 8.0° to +8.65°.

The discrepancies in the analytical data for croton oil as obtained by different observers are probably largely dependent upon the method by which the oil was obtained. Thus, Javillier[3] prepared three samples: the first by simple expression, the second by extraction with ether, and the third by digestion at 75° with 95% alcohol; the first two methods being those described by the French Codex of 1884. The yield and character of the products are shown in the following table:

	Expressed oil	Oil extracted by ether	Oil extracted by alcohol
Yield	12.5%	38%	12%
Colour	Pale.	Light brown.	Very dark brown.
Solubility (1 vol. of oil +2 vols. absolute alcohol).	Soluble at 75°	Soluble at 75°	Soluble in the cold.
Solidification temperature	−7°	−7°	−8°
Iodine number	109	108	91.2
Saponification value	192.9	194.5	260.6
Acid value	27.3	30.9	60.1

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[1] *Proc. Roy. Soc.*, 1895, 58, 238.

[2] *Chem. Zeit.*, 1906, 30, 143.

[3] *J. Pharm. Chim.*, 1898, 7, 524.

The acid value was estimated by dissolving the oil in ether and titrating directly with N/10 alcoholic potassium hydroxide.

Dulière[1] states that croton oil obtained by extraction with petroleum spirit or by cold expression has the same characteristics as the official oil, but that oils prepared by hot expression or by extraction of the non-decorticated seeds with ether, differ from it in colour, acidity, and degree of solubility in absolute alcohol, although the chief chemical constants are practically identical. He gives the following table of constants for this oil:

Sp. gr. at 15°	0.9437
Sp. gr. at 100°	0.8874
Solubility in 92% alcohol	1 in 63
Critical temperature (Crismer)	54.8°
Oleo-refractometer degrees, 22°	+35
Butyro-refractometer degrees, 27°	77.5
Acid value (Burstyn)	21.8
Saponification value	215.6
Reichert-Meissl value	12.1
Acetyl value (Lewkowitsch)	38.64
Solidifying-point of mixed fatty acids	16.4 to 16.7°

Two samples of croton oil examined by Lewkowitsch[2] gave the following results:

Saponification value	215.0	210.3
Acetyl value	19.82	32.66

The same observer[3] found 0.55% of unsaponifiable matter in several samples of croton oil and 18.6 to 19.0° as the titer test of the mixed fatty acids.

Adulteration of croton oil with castor oil would be detected by the increased acetyl value. Hydrocarbons, which are said to be frequently added (Dulière), would lower the saponification value and increase the percentage of unsaponifiable matter.

CURCAS OIL.

(See p. 71.) This is from the seeds of the "physic nut" or "purging nut" tree, *Jatropha curcas*, a plant chiefly cultivated in the Portuguese colonies, and especially in the Cape Verde Islands. It is yellowish-brown in a crude state, pale yellow when refined, has a faint unpleasant odour, and powerful purgative properties, 10 drops having a greater purgative effect than a tablespoonful of castor oil (Klein). It is only slightly soluble in alcohol, 100 volumes of absolute alcohol at 15.5° dissolving about 2.17 volumes (Archbutt[4]), and freely soluble in petroleum spirit, by which properties, together with its much lower viscosity, it is readily distinguished from castor oil.

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[1] *J. Ann. de Pharm. de Louvain*, 1899, 229 and 278.

[2] *Analyst*, 1899, **24**, 319.

[3] Oils, Fats and Waxes, II, 184.

[4] *J. Soc. Chem. Ind.*, 1898, **17**, 1009.

According to Klein,[1] curcas oil is composed of esters of solid and liquid fatty acids, the former (9 to 10%) consisting of palmitic and stearic acids and the latter of oleic and linoleic acids in about equal proportion. No ricinoleic or linoleic acid was detected.

Besides its medicinal uses, curcas oil is employed as a lamp oil, and in the manufacture of soap and candles; as a lubricant, however, for which purpose it is also said to be used, it has the disadvantage of drying nearly as rapidly as cottonseed oil. Thin films on glass dried in from 24 to 30 hours at the ordinary temperature, cottonseed oil drying under the same conditions in 18 to 20 hours, and refined rape oil in 48 hours (Archbutt).

With nitric acid (1.375), refined curcas oil gives a pale brown colour, changing to orange on standing; with Halphen's test and with furfural and hydrochloric acid it gives negative results.

Very discordant numbers for the constants of this oil have been published by different observers, which accounts for the wide range shown in the table on p. 71. The results given below were obtained by Lewkowitsch and Archbutt.

	Lewkowitsch		Archbutt.		
	Authentic sample of expressed curcas oil[2]	Commercial oil	Commercial oil from Lisbon		
			Crude	Refined	Refined
Sp. gr. at 15.5°	0.9204	0.9204	0.9205	0.9205	0.9205
Viscosity (absolute) at 15.5° (cottonseed oil 0.82—0.91)	(0.864)	......	0.858	......	0.878
Solidifying-point, °	−8°	......	......	Turbid, 4.4° Solid, 3°	......
Melting-point, °	−4°	......	......	......	......
Free (oleic) acid, %	(4.46)	......	11.8	0.26	0.47
Unsaponifiable matter, %	....	......	......	0.56	......
Maumené test, °	(65°)	......	67.5°	66.6°	......
Specific temperature test	(138)	......	144	145	......
Iodine value	98.3	100.2	98.0	99.1	100.0
Saponification value	193.2	191.2	192.8	192.9	192.2
Hehner value	95.5	95.6	......	......	95.2
Acetyl value	7.5	9.02	14.03	......	9.82
Reichert-Meissl value	0.55	0.22	......	......	0.28
Mixed Fatty Acids					
Saponification value	....	......	......	202.4	......
M. p.; °	....	......	......	27.5°	......
Solidifying-point (titer test), °	27.7°–28.6°	27.5°	......	......	......

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[1] *Zeitsch. angew. Chem.*, 1898, 1012.

[2] The numbers in parentheses are by Archbutt.

Klein obtained the following numbers in the examination of specimens of curcas oil which he extracted from the seed; sp. gr. at 15°, 0.9199 to 0.9240; refractive index at 25°, 1.4686 to 1.4689; iodine value 109.1 to 110.4; saponification value, 197.0 to 203.6; m. p. of mixed fatty acids, 29.5° to 30.5°; solidifying-point of fatty acids, 25.75° to 26.5°.

Curcas oil is said to be used as an adulterant of olive oil in Portugal, but in view of its purgative properties this seems unlikely.

GRAPE SEED OIL.

(See p. 71.) Grape seeds contain from 6 to 20% of oil, which, when obtained by cold expression from fresh seeds, is golden-yellow and sweet, but that from seeds which have been stored for some time is darker and slightly bitter. It is an edible oil. The oil from a second hot-pressing is brown, with a pronounced bitter taste; it is used, after refining, as a lamp oil.[1]

It dissolves at 70° in an equal volume of acetic acid (sp. gr. 1.0562), the solution becoming turbid at 66.5°. It is moderately soluble in alcohol. It gives the elaidin reaction. Horn has suggested that it might be used as a substitute for castor oil in Turkey-red oil manufacture. A large quantity could be obtained. The numbers given in the table on p. 71 are based upon the results obtained by Horn[2] and De Negri and Fabris.[3] The following quite different numbers have been since published by Ulzer and Zumpfe.[4]

Sp. gr. at 15°	0.9215
Butyro-refractometer reading at 50°	54.5
Refractive index	1.4623
Iodine value	142.8
Saponification value	190.0
Acetyl value of the fatty acids	43.7
Maumené value	81° to 83°

The earlier observers inferred that this oil resembles castor oil in containing a large proportion of hydroxy-acids, and that it also contains erucic acid. Ulzer and Zumpfe found it to consist chiefly of the glyceride of linolic acid, with about 10% of solid glycerides, and smaller quantities of the glycerides of oleic, ricinoleic and, linoleic acids. No erucic acid was detected. Further investigation is evidently needed

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[1] *Chem. Rev. Fett-Harz-Ind.*, 1903, **10**, 219.
[2] *Mittheil. Tech. Gerwerbe-Museums*, 1891, 185.
[3] *Ann. del. Lab. Chim. Centr. del. Gabelli*, 1891–2, 225.
[4] *Oester. Chem. Zeit.*, 1905, **8**, 121.

VI. CACAO BUTTER GROUP.

Bassia Tallow.
Borneo Tallow (Tangkawang Fat).
Cacao Butter.
Chinese Vegetable Tallow (Stillingia Tallow).
Cotton Oil "Stearine."
Goa Butter (Kokum Butter).
Laurel Oil.
Mafura Tallow.
Nutmeg Butter.
Palm Oil.
Phulwara Butter.
Piney Tallow (Malabar Tallow).
Shea Butter (Galam Butter).

BASSIA TALLOW.

(For constants see p. 71.) This fat, as met with in commerce, is a mixture of the fats obtained from the seeds of *Bassia longifolia* and of *B. latifolia*, the former being termed *Mohwah butter* or *Mowrah seed oil*, and the latter *Mahua butter* or *Illipé butter*. It is used in the manufacture of soap and candles.

BORNEO TALLOW. (TANGKAWANG FAT.)

(For constants see p. 71.) This fat is expressed from the seeds of several different kinds of plants, belonging to the order *Dipterocarpaceæ*, notably *Shorea stenoptera*, a native of Northwest Borneo. It is a greenish-yellow fat, gradually changing to white, resembling cacao butter in consistency and taste. It has a crystalline structure, and is covered with fine needles of stearic acid. It melts at 35° to 42°. According to Geitel,[1] it consists chiefly of the esters of stearic and oleic acids, but Klimont[2] has isolated from it oleodistearin and oleodipalmitin. The commercial fat has been found to contain from 8 to 10% of free (stearic) acid. It is used in Europe in the manufacture of soap and candles.

CACAO BUTTER. OIL OF THEOBROMA.

(See also page 71.) This oil is expressed from the beans or seeds of the cacao tree, *Theobroma cacao*, from which ordinary cocoa is obtained, and must not be confused with cocoanut oil from *Cocos nucifera*. It is obtained in large quantities as a by-product in the manufacture of chocolate.

[1] *J. prakt. Chem.*, 36, 515.
[2] *Monatsh. Chem.*, 1904, **25**, 929.

The percentage of cacao butter in the roasted nibs or beans has been carefully estimated by Davies and McLellan[1] by extraction of the powdered nibs with petroleum spirit. Beans from Ecuador, Venezuela, Dutch Guiana, Brazil, the West Indies, Africa, and Ceylon were examined. The average percentages of fat in the different sorts ranged from 51.33 to 58.23, the average of the whole being 54.44.

Cacao butter is a yellowish solid, gradually turning white on keeping. At the ordinary temperature it may be broken into fragments, but softens in the hand and melts in the mouth. It fuses between 30 and 34° (rarely at 29°) to a transparent yellowish liquid, which congeals agains at 20.5°, the temperature rising to about 27°. It has an agreeable odour, tastes like chocolate, and does not readily become rancid. Lewkowitsch,[2] however, has shown that cacao butter, if exposed to the combined action of sunshine, air, and moisture for a few days, becomes bleached and rancid like any other fat. It dissolves in 20 parts of hot alcohol, separating almost completely on cooling, and is also dissolved by ether and ethyl acetate. It is largely used as the fat in the manufacture of chocolate creams, and in pharmaceutical preparations and cosmetics.

Cacao butter chiefly consists of the propenyl esters of stearic, palmitic, oleic, and linolic acids. C. Kingzett[3] obtained from cacao butter an acid of the formula $C_{64}H_{128}O_2$, which he named theobromic acid, but neither Traub[4] nor Graf[5] were able to find any fatty acids of higher molecular weight than arachidic. Hehner and Mitchell[6] found 40% of stearic acid; Farnsteiner[7] obtained 59.7% of saturated acids, 31.2% of oleic acid, and 6.3% of other acids. Klimont[8] believes these acids to exist mainly in the form of mixed esters. Matthes and Rohdich[9] have found in the unsaponifiable matter two phytosterols, identical, respectively, with the sitosterol and stigmasterol isolated by Windhaus from calabar bean fat.

The following results have been obtained by examination of the mixed fatty acids of cacao butter (see also p. 71):

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[1] *J. Soc. Chem. Ind.*, 1904, **23**, 481.
[2] *J. Soc. Chem. Ind.*, 1899, **18**, 556.
[3] *J. Chem. Soc.*, Trans., 1878, **33**, 38.
[4] *Arch. Pharm.*, (3), **21**, 19.
[5] *Ibid.*, (3), **26**, 830.
[6] *Analyst*, 1896, **31**, 321.
[7] *Zeitsch. Nahr. Genussm.*, 1899, **2**, 1.
[8] *Monatsh.*, 1902, **23**, 51; 1905, **26**, 563.
[9] *Ber.*, 1908, **41**, 19.

		Observer
Solidifying-point (titer test)	48.3–49.2	Lewkowitsch.
Refractive index at 60°	1.422	Thoerner.
Neutralisation value	190	Thoerner.
Iodine value	32.6–39.1	De Negri and Fabris, Thoerner.

Cacao Butter Adulterants.—The adulterants which should be looked for in cacao butter are numerous, and include cocoanut and palm-nut oils, and the "stearines" prepared from them (a mixture of 2/3 palm-nut "stearine" and 1/3 coconut "stearine" is said to be a favourite substitute), tallow and lard, stearic acid, sesame and other vegetable oils, beeswax and paraffin wax. For the detection of these adulterants the most important estimations are the *iodine value*, *saponification value*, *Reichert-Meissl value*, *acid value*, and *sp. gr.*, together with the *m. p. of the fat and its mixed fatty acids*, or the *titer test* of the latter.

Coconut and palm-nut oils and "stearines" would lower the iodine value and sp. gr., raising at the same time the saponification value and Reichert-Meissl value. They would also lower the titer test of the fatty acids.

Tallow, beyond somewhat lowering the sp. gr., would cause scarcely any change in the other values. It may be detected by Björklund's test (see p. 179) and the phytosterol acetate test (p. 301), the latter of which would also have to be applied to for the detection of lard, although the presence of lard would have some tendency to raise the iodine value.

Stearic acid would be detected by an estimation of the acid value which, in genuine cacao butter, does not usually exceed about 2.0.

Most **vegetable oils** would lower the sp. gr. of the fat and the titer test of its mixed fatty acids, and would raise the iodine value; cottonseed and sesame oils would be detected by their characteristic colour indications, arachis oil by its arachidic acid, etc.

Beeswax and paraffin wax would be easily detected; the former would raise the acid value and m. p. of the fat, lowering at the same time the iodine and saponification values, and both beeswax and paraffin wax would increase the amount of unsaponifiable matter, which in genuine cacao butter is quite small.

According to Sachs,[1] various exotic fats have, of recent years, been used as substitutes for cacao butter in the manufacture of chocolate, the chief of these being Dika or Gaboon fat, Tangkawang fat (Borneo tallow) and Illipé fat.

Dika fat[2] resembles coconut oil in saponification value (245) and iodine value (5.2), and also in the absence of stearic acid (Lewkowitsch found no stearic acid in Dika fat and only 1%[3] in coconut oil), but it differs from coconut oil in Reichert-Wollny value (0.42%). *Borneo tallow*, according to the results obtained by Klimont,[4] closely resembles cacao butter; Illipé fat, on the other hand, has a considerably higher iodine value (53.4 to 67.9).

Sachs states that a mixture of 75% of coconut "stearine" and 25% Japan wax has given good results as a cacao butter substitute; such a mixture would have about the same m. p. as genuine cacao butter, but would be readily distinguished by the much lower iodine value and higher saponification value and Reichert-Meissl value. Posetto[5] examined a substitute of this nature, sold as "vegetable butter" or "cacao butter S." It had a faint tallow-like smell and taste, and had the following constants:

M. p.	34° to 35.5°
Iodine value	7.8
Saponification value	237.0
Reichert value	5.50
Free acid	nil

Posetto concluded that it was a mixture of coconut oil 70 to 75%, Japan wax, 30 to 25%. Another mixture said to be used is composed of 60% coconut "stearine" and 40% Borneo tallow.

Björklund's Ether Test.—3 grm. of the fat are shaken in a well-corked test-tube with twice the weight of ether at 18°. If wax be present, the solution will be turbid and will not become clear even on warming. Genuine cacao butter will dissolve to a clear solution. If a clear solution be obtained, the tube is immersed in water at 0°, and the number of minutes noted which elapse before the liquid becomes turbid, also the temperature at which the solution again becomes clear on warming. The following are Björklund's observations:

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[1] *Chem. Rev. Fett-Harz-Ind.*, 1908, **15**, 9, 30.
[2] Lewkowitsch. *Analyst*, 1905, **30**, 394.
[3] Oils, Fats and Waxes, Vol. II, p. 518.
[4] *J. Soc. Chem. Ind.*, 1904, **23**, 1152.
[5] *Giorn. di Farm. Chim.*, 1901, 337.

	Turbidity at 0° after minutes	Clear solution at 0°
Pure cacao butter	10–15	19–20
Cacao butter + 5% beef tallow	8	22
Cacao butter + 10% beef tallow	7	25

Lewkowitsch[1] found that cacao butter containing as much as 10% of tallow will dissolve in 2 parts of ether at 18°, although requiring a little longer than the genuine butter does, and that the chief indication to be relied upon is not so much the time required for crystallisation to commence, as this varies with different samples of cacao butter, but the characteristic way in which genuine cacao butter crystallises as compared with adulterated samples. With genuine samples, distinct tufts of crystals appear at the bottom and sides of the tube, whereas 5% and more of tallow are recognised by flocks separating from the chilled solution.

A method for the detection of coconut oil in butter, applicable also to lard and cacao butter, has been described by L. Robin,[2] based upon the almost complete solubility of coconut oil fatty acids in alcohol of 56.5% strength and the very slight solubility of the fatty acids from butter and cacao butter. 5 grm. of the fat are saponified by boiling for about 5 minutes with 25 c.c. of alcoholic potassium hydroxide, the operation being conducted in a flask graduated at 150 c.c. attached to a reflux condenser. After cooling, sufficient water is added to reduce the alcoholic strength to 56.5%, and a volume of N/2 hydrochloric acid (prepared with 56.5% alcohol) sufficient to exactly neutralise the alkali and liberate the fatty acids from the soap. The volume of acid required is ascertained by a previous titration. The contents of the flask are then made up to 150 c.c. at 15° with 56.5% alcohol, well mixed, allowed to stand for at least half an hour, and filtered. 50 c.c. of the filtrate are titrated with N/10 alkali, using phenolphthaleïn as indicator, and the result calculated to c.c. per 1 grm. of fat represents *fatty acids soluble in* 56.5% *alcohol.* The author of the process states that if even 5% of coconut oil is present in cacao butter, the "alcohol-soluble" number will be not less than 3, while the ratio of the alcohol-soluble number to the saponification value of the fat will be less than 60. A ratio of 45 to 60 corresponds with the presence of

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[1] *J. Soc. Chem. Ind.*, 1890, **18**, 557.
[2] *Ann. de Chim. Anal.*, 1906, **11**, 454, and **12**, 181.

5 to 10% of coconut oil, a ratio of 35 to 45 with 10 to 15%, and a ratio of 25 to 35 with 15 to 20%.

Robin's analytical results are summarised in the following table:

	Pure cacao Butter (9 samples)	Cacao butter to which cocoanut oil had been added to the extent of		
		5%	10%	15%
Saponification value (a)	191.0–195.4	195.1–199.8	199.0–204.3	205.0–205.6
Alcohol-soluble number (b)	2.30–2.81	3.56–4.10	4.50–5.47	5.76–6.79
Ratio a/b	69–84	48–55	36–45	30–35

For the detection of coconut oil by means of the "ethyl ester value" (Hanus and Stekl's method) see under "Coconut Oil," p. 187.

CHINESE VEGETABLE TALLOW (STILLINGIA TALLOW).

(For constants see p. 71.) This fat is obtained from the fruits of a variety of plants, the most important of which is the Chinese tallow tree, *Stillingia sebifera* (*Croton sebiferum L.*). It is largely employed in the manufacture of soap and candles.

The fat is found as a coating about 0.5 mm. thick on the seeds, from which it is melted by steam heat. The seeds themselves contain a strongly drying oil (stillingia oil) of quite a different character from the fat which coats them, and some of this is liable to be contained in the commercial tallow. Its presence would be shown by its high iodine value and rotatory power on polarised light.

Commercial Chinese vegetable tallow is a white or greenish fat, without taste or smell, the analytical values of which vary considerably owing to its being obtained from different plants and prepared in different ways. It is believed to consist of esters of palmitin and olein, and these exist, according to Klimont,[1] partly as the mixed ester oleodipalmitin. A sample tested by Hehner and Mitchell contained no stearin. Valenta, by the lead-salt-ether method, obtained 35.56% of oleic acid and 64.44% of palmitic acid.

COTTON OIL "STEARINE."

This is the name given to the soft solid fat that separates when cottonseed oil is chilled. It is utilised in the manufacture of margarine and of soap. It consists chiefly of palmitin and a little stearin, with olein and linolin (see "Cottonseed Oil").

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[1] *Monatsh. Chem.*, 1903, 24, 408.

GOA BUTTER (KOKUM BUTTER, MANGOSTEEN OIL).

(For constants see p. 71.) This fat is expressed from the seeds of the East Indian plant, *Garcinia indica.* It is used locally as a food, while the commercial product is manufactured into soap. It consists chiefly of the mixed glyceride, oleo-distearin (Heise).

LAUREL OIL.

(For constants see p. 71.) This is a butter-like fat of greenish-yellow colour, slightly bitter taste, and peculiar aromatic odour, obtained from the berries of the laurel tree, *Laurus nobilis*, which yield about 25%. It consists largely of trilaurin, with probably a small amount of olein and linolin. It is employed in the preparation of veterinary medicines.

MAFURA TALLOW.

(For constants see p. 71.) This is a light yellow fat obtained from the seeds of *Mafureira oleifera.* It consists of glycerides of solid fatty acids (71.4%) and of liquid fatty acids (23%) (De Negri and Fabris). It is used in the manufacture of soap and candles.

NUTMEG BUTTER.

(For constants see p. 71.) This is a yellow tallow-like fat obtained from the seeds of the *Myristica officinalis*, the yield being about 20 to 25%. As expressed, it consists of a fixed oil with 8 to 10% of an essential oil (nutmeg oil). The glyceridic portion is composed chiefly of myristin and olein, with a small proportion of butyrin (Jean). The fat is used in the manufacture of perfumes and for medicinal preparations.

PALM OIL.

(See also page 71.) Palm oil is the product of several species of palm, but particularly of *Elais guineenis* and *E. melanocca.* The former is indigenous to tropical W. Africa, and forms vast forests whence the European supply of palm oil is derived; *E. melanocca* is cultivated in S. America and the W. Indies. Palm oil proper is obtained from the outer fleshy coating of the seed, the palm-nut or palm-kernel oil having a different composition.

Palm oil varies in consistency from that of soft lard to that of the hardest tallow, and its m. p. is correspondingly variable. Soft oil is obtained from the fresh fruit, hard oil from fruit which has been stored in the ground and has undergone fermentation. Hard oil, besides being much decomposed and more or less dark in colour, usually contains dirt which has become mixed with the fruit during storage. Pure fresh palm oil has an agreeable and quite characteristic smell, and is of a bright orange colour; but the oil of commerce, owing to the crude method of manufacture, often has a "stink almost indescribable" and every shade of colour between golden-yellow and black. Inferior kinds are further deteriorated by adulteration, a fine red earth being used at Saltpond and overripe plantains and sour "kanki" in the Chama district of the Gold Coast.[1] Lagos furnishes the purest and most highly valued palm oil for some purposes, Accra and Saltpond inferior and less valuable sorts.

The colour of commercial palm oil becomes pale after keeping, especially upon exposure to light and air, the oil at the same time becoming rancid; but refined neutral palm oil may be kept for years without developing acidity or rancidity.

Palm oil is eaten as butter by the natives of the Gold Coast, and is used for anointing their bodies. In this country it is used for the manufacture of soap and candles, and in the manufacture of tin-plates in S. Wales. It is also a common ingredient of railway wagon-axle greases. It is used in the United States for colouring butter substitutes. (See p. 310.)

In chemical composition palm oil consists essentially of palmitin, olein, and free palmitic acid, with small quantities of stearin, linolein, and another fat. According to Nordlinger,[2] the solid fatty acids contain 98% palmitic acid, 1% stearic acid and 1% heptadecylic acid, the latter having been since resolved by Holde[3] into palmitic acid and an acid of much higher molecular weight.

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[1] *Kew Bulletin*, July, 1891, on "African Palm Oil." See *J. Soc. Chem. Ind.*, 1891, 10, 707.

[2] *J. Soc. Chem. Ind.*, 1892, 11, 445.

[3] *Ber.*, 1905, 38, 1247.

The following results have been obtained by examination of the mixed fatty acids of palm oil:

		Observer
Sp. gr. at 98°–99°/15.5°	0.8369	Allen.
Sp. gr. at 100°/100°	0.8701	Archbutt.
Solidifying-point (titer test)	35.8°–47.6°; usually 44°–45°	Various.
Iodine value	53.3	Thoerner.
	49.2–58.9	Tipler.[1]
Iodine value of liquid fatty acids	95–99	Lewkowitsch, Tolman and Munson.

Commercial Palm Oil.

Palm oil as met with in commerce varies greatly in quality. It almost always contains more or less water and solid impurities. Some of the irregular oils occasionally contain 25 or 30%, but the usual range is from 2 to 16%, while most of the regular oil does not contain more than 5 or 6%. It is usual to sell palm oil on the assumption that 2% of such foreign matters are present; any excess over this is allowed for.

Water is best estimated by exposing 10 grm. of the sample to a temperature of 110° for an hour or two, and noting the loss of weight (see "Lard"). If the residual oil be then dissolved in warm petroleum spirit, the *solid impurities* will settle to the bottom, and can be filtered off, washed with a little ether, dried, removed from the filter, and weighed. After weighing, the residue may be ignited, when the ash will indicate with sufficient accuracy the proportion of *sand* and mineral matters, and loss of weight will give that of the *organic matter*. In many cases the water can be estimated with sufficient accuracy by noting the measure of the aqueous layer which separates when the undried sample is dissolved in petroleum spirit, or simply kept melted in a graduated tube immersed in hot water.

Palm oil is not, as a rule, adulterated with other fats, but it frequently contains a large proportion of *free fatty acids*. The free acid raises the solidifying-point of the oil, and causes it to have a corrosive action upon iron and steel, especially in the presence of water. Axle grease made from acid palm oil may seriously pit and corrode the metal of bearings and journals, unless the free acid be neutralised.[1]

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[1] 14 samples, see p. 186, omiting two very acid and rancid oils which absorbed only 23.7 and 33.3%, respectively.

The following proportions of free fatty acid, calculated as palmitic, have been found in palm oil:

Kind of oil	Palmitic acid, %		Kind of oil	Palmitic acids, %
	Archbutt	A. N. Tate		L. Archbutt
Saltpond	78.9	84.0	Fernando Po	40.5
Unknown	72.0	....	Half-jack	35.7
Refined	55.8	....	Half-jack	24.4
Brass	53.2	65.0	Bonny	21.5
New Calabar	52.2	49.0	Lagos	11.9

Lewkowitsch states that he has found from 50 to 70% of free (palmitic acid in a large number of commercial palm oils.

The following results obtained by the analysis of typical samples of palm oil, from which the water and impurities were removed, were communicated to Allen by A. Norman Tate:

	Brass	Benin	Lagos	New Calabar	Old Calabar	Grand Bassa
Sp. gr. at 15°	.9213	.9228	.9203	.9269	.9209	.9245
Saponification value	200.2	198.3	196.6	199.7	197.2	201.2
Fatty acids, %	96–97	96–96.5	94–97	94–97	94.2–95	95.5–96.5
Fatty acids; solidifying point.	44.4–45.8	45.0–45.5	44.5–45.5	44.2–45.5	44.2–45.5	41.5–42.3
Fatty acids; combining weight.	273.4	273.7	272.7	273.2	273.2	273.0

Analyses of 16 samples, representing various brands of palm oil, recently made by Mr. F. C. Tipler, chemist of the London and North Western Railway Co., and kindly communicated by him, are given in the table on p. 185.

Palm olein is obtained by subjecting palm oil to hydraulic pressure in the same way that lard oil is made from lard. It usually has a sp. gr. of about 0.914, and solidifies at 10°.

See Archbutt and Deeley. Lubrication and Lubricants, p. 214.

ANALYSES OF PALM OIL (*Tipler*).

Description	Lagos	Emoe.	Qua Eboe	Bonny	Old Calabar	Benin	Forcados	Victoria	Cameroon	New Calabar	Accra	Half Jack	Red Sierra Leone	Congo	Salt pond	Bassa
Colour	Orange yellow	Orange yellow	Orange yellow	Orange yellow	Orange yellow	Yellow	Yellow	Orange yellow	Brownish yellow	Greenish yellow	Light brownish yellow	Deep orange yellow	Deep orange yellow	Dirty yellowish brown	Light brownish yellow	Dirty greenish yellow
Odour	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Rancid	Very rancid	Satisfactory	Satisfactory	Very rancid and objectionable	Rancid and sickly	Fairly satisfactory
Water (loss at 105°–110°)	0.55%	0.77%	0.17%	0.59%	0.75%	1.61%	1.43%	1.00%	0.81%	1.20%	1.45%	2.49%	1.31%	2.18%	1.78%	3.98%
Matter insoluble in ether	0.015%	0.079%	0.008%	0.116%	0.180%	0.319%	0.084%	0.016%	0.069%	0.239%	0.114%	0.175%	0.081%	0.246%	0.041%	1.040%
Containing ash	0.004%	0.056%	0.002%	0.062%	0.037%	0.267%	0.057%	0.005%	0.004%	0.133%	0.075%	0.104%	0.018%	0.237%	0.023%	0.433%
Specific gravity at 100°/100°	0.8718	0.8774	0.8713	0.8717	0.8702	0.8720	0.8720	0.8725	0.8713	0.8724	0.8735	0.8713	0.8711	0.8794	0.8897	0.8747
M. p., ° (Bensemann's method) Incipient fusion	25°	32°	28°	34°	28°	34°	40°	32°	30°	42°	35°	23°	30°	45°	46.5°	43°
M. p., ° (Bensemann's method) Complete fusion	42°–45°	49°	48°	51°	48°	49°	50°	52°	50°	51°	51°	48°	50°	55°–60°	55°–60°	55°–60°
														Insoluble matter interferes.		
Free (palmitic) acid	11.26%	24.58%	9.22%	10.24%	24.58%	37.89%	36.86%	18.94%	17.92%	48.13%	36.86%	21.50%	21.50%	76.29%	83.46%	70.14%
Saponification value, %	19.0	19.5	19.3	19.3	19.8	19.6	19.9	19.5	19.4	19.6	19.6	19.5	18.9	20.1	20.4	19.6
Iodine value (Wijs)	57.5	53.0	56.5	53.7	53.0	52.0	52.5	53.5	53.7	50.2	54.7	56.7	55.7	33.0	20.4	48.7
Mixed Fatty Acids																
Iodine value	58.3	50.2	58.3	55.0	55.0	53.2	50.2	50.3	53.7	53.5	49.2	56.5	54.7	33.3	23.7	49.9
Titer test, °	44.0°	42.3°	43.9°	44.3°	44.6°	44.6°	44.7°	44.8°	44.6°	44.9°	44.1°	40.4°	43.0°	47.0°	47.6°	40.9°

PHULWARA BUTTER.

(For constants see p. 71.) This fat is derived from the seeds of the Indian butter tree, *Bassia butyracea.* It is used locally as a food, while the exported product is made into soap.

PINEY TALLOW (MALABAR TALLOW).

(For constants see p. 71.) This is a light green fat obtained from the seeds of the Indian plant, *Vateria indica.* It is used for illuminating purposes, and in the manufacture of soap.

SHEA BUTTER (GALAM BUTTER).

(For constants see p. 71.) This is a butter-like, grayish-white fat, obtained from the seeds of *Bassia Parkii*, used in the manufacture of soap and candles.

VII. COCONUT OIL GROUP.

Coconut Oil. **Macassar Oil.**
Japan Wax. **Myrtle Wax.**
Palm-nut Oil. **Palm-kernel Oil.**

COCONUT OIL.

(See also p. 72.) Coconut oil is obtained by expression or extraction from the white pulp ("copra") of the common coconut, the seed of *Cocos nucifera* and *C. butyracea.* It is a white or but slightly coloured fat, having the characteristic odour and taste of coconut, and the consistence of butter or soft lard. The commercial product easily becomes acid and rancid, and then has a bad taste and odour. If properly prepared, however, it is equal in neutrality and keeping qualities to other oils and fats, and it does not become rancid any sooner than other fats if properly stored in full vessels protected from light and air.[1] The excessive acidity met with in commercial samples is frequently developed in the fat previous to its expression from the copra, through the latter being allowed to ferment, as in the case of palm oil and other fats. Lewkowitsch has found from 5% to 25% of free fatty acid, calculated as oleic acid. The sp. gr. of coconut oil is higher than that of the majority of vegetable fats. Allen observed a range of from 0.868 to 0.874 at $\frac{98^\circ-99^\circ}{15.5^\circ}$; Crossley and Le Sueur obtained values from 0.903 to 0.9042 at $\frac{100^\circ}{100^\circ}$.

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[1] *J. Soc. Chem. Ind.*, 1906, 25, 381.

Coconut oil has a peculiar and highly complex chemical composition. It is chiefly composed of laurin and myristin, but contains also six other glycerides, including caproin, caprylin, caprin, palmitin, stearin and olein.[1] Very little stearin is present; Lewkowitsch found only 0.99% of stearic acid,[2] Hehner and Mitchell none. The volatile acids are chiefly capric and caprylic.

Coconut oil is used for candle- and soap-making. It is an excellent illuminant, emitting no smoke, and is largely used for making night-lights. It forms a hard and white soap, the aqueous solution of which is not readily precipitated by common salt; hence this soap is available for use with sea-water (marine soap).

Coconut oil and the "stearine" made from it are also used as substitutes for and adulterants of butter, lard, and cacao butter. By treatment with alcohol and animal charcoal a neutral coconut oil is produced, which is sold under such names as "vegetable butter," "vegetaline," "lactine," "nucoline," "laureol," etc. When well prepared, these products are white, of about the consistence of butter, of agreeable, sweet flavour, and, according to Jean,[3] free from tendency to become rancid. Coconut oil is frequently used in the preparation of margarine.

Coconut "oleine" is used as a lubricant, usually as an ingredient of blended oils.

The data given below and on p. 72 have been obtained from the mixed fatty acids of coconut oil:

		Observer
Sp. gr. at 98°–99°/15.5°	0.8354	Allen.
Solidifying-point (titer test)	21.2°–25.2°	Lewkowitsch.
Refractive index at 60°	1.4295	Thoerner.
Saponification value	258	Thoerner.
Mean combining weight	196–204	Alder Wright.
Iodine value	8.4–9.3	Various.

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[1] See Ulzer, *Chem. Rev. Fett-Harz-Ind.*, **6**, 203; Blumenjeld and Seidel, *J. Soc. Chem. Ind.*, 1900, **19**, 914; Jensen, *Zeitsch. Narh. Genussm.*, 1905, **10**, 265; Haller and Youssoufian *Compt. rend.*, 1906, **143**, 803; Paulmeyer, *J. Soc. Chem. Ind.*, 1907, **26**, 881.

[2] Oils, Fats and Waxes, II, 518.

[3] *Jour. Soc. Chem. Ind.*, 1891, **10**, 275.

Coconut oil is alleged to be liable to adulteration with suet, beef marrow, and other animal greases, as also with almond oil and wax. These would be detected by the reduced sp. gr. at the temperature of boiling water and the reduced saponification and Reichert-Meissl values. Indeed, there is no addition likely to be made in practice, excepting that of palm-nut oil, which, if in notable proportion, would not be detected by these tests. The same methods, if used with discretion, will equally serve to estimate the approximate proportion of the adulterant. *Palm-nut oil* cannot be detected by the above or any other satisfactory method, but as it is employed for the same purposes as coconut oil, the substitution has little practical importance.

Hanus and Stekl[1] have proposed a new constant for the detection of coconut oil in other oils and fats, which they name the "ethyl-ester value." 5 grm. of the melted and filtered fat are weighed into an Erlenmeyer flask of about 200 c.c. capacity (14 cm. high and 7 cm. wide) heated for 15 minutes in a thermostat at 50°, then rapidly mixed with 30 c.c. of N/10 alcoholic potassium hydroxide, vigorously shaken until quite clear, and again heated in the thermostat until the lapse of 10 minutes from the time of adding the alkali. To the liquid is next added 2 c.c. of dilute sulphuric acid of such strength as to exactly neutralise the 30 c.c. of alkali, sufficient water to make the volume up to 140 c.c., and a few fragments of pumice stone. The flask is fitted with a cork and bulb tube, connected to an inclined condenser 70 cm. long, and the liquid rapidly distilled. The first 30 c.c. of alcoholic distillate are collected in a graduated cylinder, and the next 100 c.c. of aqueous distillate in a 100 c.c. flask. The distillation should be finished within 25 minutes. The latter (aqueous) fraction is rinsed into an Erlenmeyer flask, sufficient alcohol being used to bring the esters into solution, the free fatty acids are neutralised, and the esters are saponified by heating for about 45 minutes under a reflux condenser with 40 c.c. of N/2 alcoholic potassium hydroxide. When cold, the excess of alkali is titrated with N/10 hydrochloric acid, the result giving the number of c.c. of N/10 alkali required to saponify the respective esters from 5 grm. of fat. The "ethyl-ester values" of the following fats were determined:

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[1] *Zeitsch. Nahr. Genussm.*, 1908, 15, 577.

	Ethyl-ester value
Coconut oil, 5 samples	41.45 to 45.30
Palm-nut oil, 1 sample	23.15
Cows' butter, 15 samples	7.1 to 13.4
Margarine, 5 samples	1.70 to 3.00
Lard, 4 samples	2.70 to 3.20
Cacao butter, 3 samples	1.30 to 1.60

It appears from these results that the method is capable of detecting a small percentage of coconut oil in margarine, lard, or cacao butter, but not less than 15% could be detected in cows' butter. If coconut oil alone be present, the numbers afford a means of approximately estimating the proportion, but the presence of palm-nut oil would upset the calculation.

Coconut "oleine" and coconut "stearine" are products obtained by submitting coconut oil to hydraulic pressure. The following figures, obtained in Allen's laboratory from samples supplied to him by Price's Patent Candle Company, show the relative physical and chemical characters of the two products:

	Oleine	Stearine
Sp. gr. at $\frac{98.5^\circ}{15.5^\circ}$	0.8710	0.8696
Sp. gr. at $\frac{60.^\circ}{15.5^\circ}$	....	0.8959
Sp. gr. at 15.5°	0.9262	solid
M. p.	....	28.5°
Solidifying-point	4°, rising to 8°	21.5°, rising to 26°
Saponification value	261	259
Reichert value	5.6	3.1

Sachs[1] obtained the following values from a sample of commercial hard coconut "stearine," said to be a favourite substitute for cacao butter.

Sp. gr. at 100°	0.8700
M. p.	29.3°–29.5°
Solidifying-point	26.5°
Saponification value	252
Iodine value	4.01–4.51
Reichert-Meissl value	3.4

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[1] *Chem. Rev. Fett-Harz-Ind.*, 1908, **15**, 9, 30.

Mixed Fatty Acids.

M. p.	28.1°
Solidifying-point	27.4°
Mean molecular weight	209

The following results were obtained by Archbutt in the examination of a sample of commercial coconut "oleine."

Sp. gr. at 15.5°	0.9290
Sp. gr. at 100°/100°	0.8958
M. p.	18°
Solidifying-point (titer test)	11°, rising to 13°
Viscosity (absolute) at 15.5°	0.68 (rape oil, 1.15)
Viscosity (absolute) at 100°	0.052 (rape oil, 0.086)
Saponification value	257.7
Iodine value	13.4
Free (oleic) acid	0.2%
Unsaponifiable matter	2.6%

JAPAN WAX.

(See also p. 72.) Japan "wax" is a fat contained between the kernel and outer skin of the berries of several species of *Rhus*, the most important of which are *Rhus succedanea* and *R. vernicifera*, which flourish chiefly in the western provinces of Japan, and are now also cultivated in California.

The wax is extracted by steaming and pressing the crushed berries, after separating the husk, the flow of the last portions of wax being sometimes accelerated by the addition of a little oil of Perilla. The berries yield in this process about 15% of a coarse, greenish, tallow-like mass, which is refined by melting, pressing through strong cotton sacks and allowing to drop into cold water. The flakes of wax thus obtained are bleached in the sun and, if necessary, remelted. Ahrens and Hett obtained 25% of fat by boiling the berries with water and finally extracting by ether.

The purified fat is a yellowish-white, straw-yellow, or greenish-yellow, wax-like, mass, having a smell recalling at once that of tallow and of some kinds of beeswax. Under ordinary circumstances it fuses at 51° to 53°, but a recently solidified sample melts at a considerably lower temperature. Its solidifying point is about 41°, the temperature rising to 48 to 49° in the act of solidification.

The sp. gr. at the ordinary temperature is about 0.990, while in a molten state at a temperature of 98° to 99° it is 0.875 to 0.877, compared with water at 15.5°. Thus, in the solid state it agrees in specific gravity with the true waxes, and in the molten state it is considerably heavier than the true waxes or the ordinary vegetable fats.

Kleinstück,[1] who investigated the subject minutely, found that the closeness with which the sp. gr. of Japan wax approximates to that of water, coupled with its high coefficient of expansion, gives rise to the curious phenomenon of its floating in water at temperatures above 18°, and sinking below 15°. This behaviour is, however, modified by the fact that, like other similar substances, it is at first abnormally light after being melted and allowed to solidify, regaining its normal sp. gr. only after some time. The following table gives Kleinstück's results:

Temperature, °	Sp. gr. compared with water at 4°		
	Japan wax		Water
	Of normal sp. gr.	After recent fusion	
6.5	....	1.00237	0.99995
7.2	1.00737	....	0.99991
17.0	....	0.99123	0.99884
17.5	0.99846	....	0.99875
23.0	....	0.98747	0.99762
26.5	0.98615	0.98683	0.99674

Japan wax is completely soluble in boiling alcohol, but is almost completely deposited on cooling. The variable hardness of the commercial wax is said to be due to the presence of the oil of perilla used in its extraction. This will also influence the iodine value, since oil of perilla is a strongly drying oil having an iodine value of 206.

Japan wax is readily and completely saponifiable, yielding glycerol, and hence is distinct in constitution from the true waxes, which yield monatomic alcohols when saponified (p. 67). It is composed chiefly of palmitin and more or less free palmitic acid. It also contains small quantities of saturated di-carboxylic acids of high m. p., of which an acid having the formula $C_{19}H_{38}(COOH)_2$, melting at 117°–117.5°, and its two lower homologues have been identified by Schaal.[2] The acid melting at 117°, to which they attributed the formula $C_{20}H_{40}$-$(COOH)_2$ and named "Japanic acid," had previously been isolated by Geitel and Van der Want[1] and found to exist in combination with palmitic acid as a mixed glyceride. The latter observers also found a small quantity of oleic acid, and about 5 to 6% of soluble fatty acids which, in their opinion, had been produced by the action of the oxidising agents used to bleach the wax.

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[1] *Chem. Zeit.*, 1890, **14**, 1303.
[2] *Ber.*, 1907, **40**, 4784.

From 5.4 to 14.9% of free (palmitic) acid have been found in commercial Japan wax. Ahrens and Hett found from 5.1 to 5.5% in wax which they extracted in the laboratory.

The following results have been obtained by the examination of Japan wax and its fatty acids, in addition to those given in the table on p. 72:

		Authority
Unsaponifiable matter, %	1.48 to 1.63	Geitel and Van der Want.
Glycerol, %	11.59; 13.50; 14.71	Allen.
Glycerol, %	10.9	Mitchell.
Fatty acids, insoluble, %	90.62; 90.66	Geitel and Van der Want.
Fatty acids, soluble, %	5.96; 4.66	
Fatty acids, soluble, %	8.40	Allen.
Properties of Insoluble Fatty Acids.		
Sp. gr. at 98 to 99°/15.5°	0.848	Allen.
M. p.	56° to 57°	Allen.
Solidifying-point	53° to 56.5°	Allen.
Combining weight	257.5 to 259.3	Allen.

That the constitution of Japan wax is peculiar is evident from the study of the products of its saponification, and is shown also by its high sp. gr. both in the solid and liquid state, in which characters it differs widely from the majority of solid fats. The sp. gr. of the insoluble acids, considered in conjunction with their mean combining weight, renders it doubtful whether these fatty acids really consist of palmitic acid, and it may be noted that Hehner and Mitchell in working out their process for the estimation of stearic acid in fats found that the fatty acids prepared from Japan wax, while possessing apparently the properties of palmitic acid, prevented the crystallisation of stearic acid in an anomalous manner. The percentage of glycerol produced by saponification of the wax, as estimated by the permanganate process in two of the samples examined by Allen, is notably in excess of that yielded by tripalmitin, especially in the sample which gave the highest result, the glycerol from which sample was estimated several times with great care. Whether this high proportion was real or due to some unusual constituent which rendered the estimation by permanganate inaccurate was not ascertained. Any considerable proportion of a diglyceride containing palmitin and a dibasic acid would raise the proportion of glycerol and would also explain the relatively low combining weight of the insoluble fatty acids.

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[1] *J. für. prakt. Chem.*, 1900, 61, 151.

Japan wax is stated to be frequently adulterated with water, with which it is capable of forming a sort of emulsion when the two are agitated together a little above the m. p. of the wax.

La Wall[1] found a number of samples adulterated with 20 to 25% of starchy matter. The sp. gr. of the adulterated wax was only slightly higher than that of the genuine article. Such adulteration would be readily detected by means of ether in which the wax would dissolve leaving the starch.

The addition of tallow would be detected by the lowered m. p. and increased iodine value; in fact, the characteristic properties of Japan wax would render the detection of adulteration easy.

MACASSAR OIL.

(For constants see page 72.) Macassar oil is a soft fat, forming 60 to 70% of the seed-kernels of *Schleichera trijuga*, a tree growing in India and the East Indies. It is used locally for cooking, illuminating, and medicinal purposes, and has long been esteemed in Europe as a valuable hair restorer. It consists of esters of lauric, palmitic, arachidic and oleic acids, with small quantities of acetic and butyric acids. Its odour is largely due to the presence of a small amount (0.03 to 0.05%) of hydrocyanic acid.

Wijs found 3.12% of unsaponifiable matter in this fat. Of the non-volatile fatty acids, 45% were saturated and 55% unsaturated (liquid) acids; the latter had an iodine value of 103.2. v. Itallie found the sp. gr. of the mixed insoluble fatty acids 0.922 at 15°.

MYRTLE WAX.

(For constants see page 72.) This is a greenish-white fat, of wax-like appearance, separated from the berries of different kinds of *Myrica* (*M. cerifera*, *M. caroliensis*, etc.). It contains myristin, palmitin, and olein, palmitic acid being the predominating fatty acid. Besides the figures on page 72, the following have been published:

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[1] *Amer. J. Pharm.*, 69, 18.
[2] *Analyst*, 1896, 21, 328.

	Smith and Wade	Allen
Sp. gr. of solid fat at $\frac{22^\circ}{15.5^\circ}$	0.9806	....
Solidifying-point	45°	39.5°
Refractive index, 80°	1.4363	....
Acid value	30.7	....
Free (palmitic) acid, %	....	0.12
Glycerol, %	....	13.38
Mixed Insoluble Fatty Acids.		
Sp. gr. at 98–99°/15.5°	....	0.837
Solidifying-point	....	46°
Combining weight	....	243.0

PALM-NUT OIL. PALM-KERNEL OIL.

(See also page 72.) This oil is obtained by expression or extraction from the fruit-kernels or nuts of the oil-palm, and is entirely different in composition from palm oil (page 182) which is obtained from the fleshy covering of the nuts.

Palm-nut oil varies from white to primrose-yellow or pink in colour, with a characteristic odour recalling that of violets, but not unlike that of coconut oil, which it resembles closely in every respect. The sp. gr. is high, ranging from 0.866 to 0.873 at 99° (compared with water at 15.5°). The m. p. is from 26° to 30°, solidification occurring at 18° to 20°, and the temperature again rising pretty constantly to 25° or 26°.

Palm-nut oil contains a large proportion of esters of lower fatty acids, the composition of a sample analysed by Oudemans[1] being given as:

Olein	26.6%
Stearin, palmitin, and myristin	33.0%
Laurin, caprin, caprylin, and caproin	40.4%
	100.0%

Valenta[2] found the oil to be composed of the same esters as stated by Oudemans, omitting stearin, but that present in largest proportion was found to be laurin. Blumenjeld and Seidel found 4.53% of volatile fatty acids capable of distillation in a current of steam.[3]

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[1] *Jour. prakt. Chem.*, [2], **11**, 393; Watts Dict. of Chemistry, **7**, 890.
[2] *J. Soc. Chem. Ind.*, 1889, **8**, 806.
[3] *J. Soc. Chem. Ind.*, 1900, **19**, 914.

It is worthy of notice that all the fatty acids of which the esters are said to be present contain an even number of carbon atoms. The same remark applies to coconut oil, which has a very similar composition (see page 188), but usually contains a larger proportion of lower fatty acids. Thus, the saponification value of palm-nut oil is usually about 247, but differs somewhat with the mode of preparation. If it be extracted from the palm-kernels by a solvent instead of by pressure, the proportion of higher fatty acids is increased, and the m. p. and saponification value of the product are respectively raised and lowered in proportion. Palm-nut oil is stated to be sometimes adulterated with, or substituted by, lard or tallow, coloured with turmeric and scented with orris root. With modified figures for the saponification value and distillate-acidity, the method of examining coconut oil for such adulterants fully applies to palm-nut oil.

Palm-nut oil is largely used for soap-making, mixed with other fats. The commercial oil contains free fatty acids, sometimes in very large proportion. Valenta found from 7 to 58% in different samples.

The mixed fatty acids of palm-nut oil have given the following results (see also page 72):

		Observer
Solidifying-point (titer test)	20 to 25.5°	Lewkowitsch.
Refractive index at 60°	1.431	Thoerner.
Iodine value	12.0	Thoerner.

Sachs[1] obtained the following results by examination of *palm-nut* "stearine," which is used, in admixture with other vegetable fats, as a substitute for cacao butter:

Sp. gr. at 100°	0.8700
Solidifying-point	28°
M. p.	31.5 to 32°
Saponification Value	242
Iodine value	8
Reichert-Meissl value	2.2

Mixed Fatty Acids.

M. p.	28.5°–29.5°
Solidifying-point	28.5°
Mean molecular weight	211

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[1] *Chem. Rev. Fett-Harz-Ind.*, 1908, 15, 9, 30.

VIII. LARD OIL GROUP.

Lard Oil.	**Tallow Oil.**
Neatsfoots Oil.	**Egg Oil.**

LARD OIL.

(See p. 72.) Lard, especially the softer kind, subjected to hydraulic pressure yields a considerable quantity of fluid called "lard oil," or "lard olein," while the solid portion constitutes "pressed lard," or "lard stearin." Consequently, the m. p. and other characters of lard oil depend much on the temperature at which the pressing is conducted, winter-pressed lard oil naturally containing less of the solid constituents of lard than that expressed at a higher temperature.

Prime lard oil is a nearly colourless, pale yellow or greenish coloured oil, having but little odour, and composed of the esters of chiefly oleic, stearic, and palmitic acids, with some linolic and perhaps linolenic acids. It usually thickens at about 4°, and becomes solid ta −4°, but some samples exhibit wide departures from these limits. A specimen of pure winter-pressed oil examined by Henry began to deposit flakes at −8°, was thick at −10°, and solid at −12°. It did not remelt completely until the temperature reached +7°. On the other hand, a sample tested by Duyk[1] began to crystallise at +10°. Commercial lard oil varies in character from the nearly neutral sweet oil above described to the acid, rancid, and offensive-smelling lard oils of deep brown colour called "Extra No. 1," "Extra No. 2," and "Extra No. 3" (Schweitzer and Lungwitz).

In many of its indications lard oil closely resembles olive oil, which it simulates in its behaviour with nitric acid, the elaidin-test, and the temperature produced by strong sulphuric acid.

Lard oil is extensively employed as a lubricant. The chief adulterants affect its viscosity and non-drying characters, and therefore its value for lubricating. Lard oil is often employed in lighthouse and signal lamps, and a small percentage of free acid or of cottonseed oil affects, injuriously, its quality for these purposes.

The *acidity* of lard oil, calculated as oleic acid, should not exceed 2%. Of 47 samples tested by Jenkins,[2] 40 satisfied this condition, and the average acidity of the whole was 1.56%.

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[1] *Bull. de l'Assoc. Belge*, 1901, 15, 18.

[2] Private communication.

10 samples contained between 0 and 1%.
30 samples contained between 1 and 2%.
5 samples contained between 2 and 3%.
2 samples contained between 4 and 6%.

Of 14 samples examined by Archbutt,

1 sample contained 0.85%.
11 samples contained from 1.0 to 2.0%.
2 samples contained 6.7%.

4 samples examined by Tolman and Munson contained from 0.28 to 1.28, and 4 by Sherman and Snell from 0.74 to 2.64% of free oleic acid.

The *sp. gr.* of genuine American lard oil at 15.5° ranges from 0.913 to 0.919, according to Schweitzer and Lungwitz,[1] and the results published by other chemists fall within these limits. Of 47 samples of commercial lard oil examined by Jenkins and believed to be genuine, only one sample had a higher sp. gr. (0.921); the remainder ranged from 0.914 to 0.919, the average being 0.9172. Adulterants, such as cottonseed oil, maize oil, and fish oils, would raise the sp. gr.

The *oleo-refractometer* is a valuable instrument for examining lard oil, the recorded deviation caused by which ranges from −1° to +5.5°. All fixed oils likely to be added as adulterants, except arachis, neatsfoot, and tallow oils, would increase the refraction (see page 44).

The average *viscosity* of commercial lard oil is about the same as that of olive oil, but it varies between rather wide limits. The efflux time of 45 samples examined by Jenkins ranged from 356 to 534 seconds for 50 c.c. at 15.5° from Redwood's viscometer, the average being 437 seconds. Olive oil from the same viscometer at 15.5° required 426 seconds. The majority of the samples fell within a narrower range, as is shown below.

6 required from 356–399 seconds.
9 required from 400–422 .5 seconds.
17 required from 427–449 seconds.
7 required from 451–466 seconds.
3 required from 477–495 seconds.
3 required from 508–534 seconds.

The *Maumené thermal value* (50 c.c. of oil and 10 c.c. of 97% sulphuric acid) ranges from about 40° to 46°, practically the same as in the case of olive oil. This is, therefore, a valuable test, since most yils likely to be added as adulterants would increase the temperature indication.

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[1] *J. Soc. Chem. Ind.*, 1895, 14, 129.

The *iodine value* of genuine lard oil depends largely on the proportion of olein. The interpretation to be placed upon the result of this test must, therefore, depend upon the congealing-point of the oil. Schweitzer and Lungwitz, who have investigated this relation, ascertain the congealing-point as follows: The oil is poured into a wide-mouthed bottle, immersed in a freezing-mixture of ice and salt, and stirred vigorously with a thermometer; the temperature is noted at which the oil shows the first sign of becoming cloudy. Any (American) lard oil with higher iodine value than 70 should not show signs of cloudiness above 40° F. The lard oils having iodine values of from 60 to 70 are generally pasty at 40° F.

The following table is taken from Schweitzer and Lungwitz's paper:

Sp. gr. at 15°/4°	Iodine value	Congealing-point
0.9136	78.8	25° F.
0.9146	76.4	28° F.
0.9174	76.0	28° F.
0.9151	71.5	35° F.
0.9159	67.8	40° F.
0.9160	63.9	42° F.
0.9186	62.8	Solid at 40° F.

Probably the iodine values of most genuine lard oils would fall between 67 and 82.

The *saponification value* is about 193 to 198. Adulteration with rosin oil, mineral oil, or rape oil would lower this value. Rosin oil or mineral oil, if present, would be found in the *unsaponifiable matter* which, in genuine lard oil, does not exceed about 0.6%.

The *flashing-point* (closed test) of a genuine sample of lard oil was found by Jenkins to be 480° F.

The *titer test* of the mixed fatty acids ranged from 27° to 33° in 46 samples examined by Jenkins, and Duyk[1] found the sp. gr. at 100° to be 0.885.

4 samples of genuine lard oil examined by Tolman and Munson (*Bull.* No. 77, United States Dept. of Agriculture) gave the following results:

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[1] *Bull. de l'Assoc. Belge*, 1901, **15**, 18.

	1	2	3	4
Sp. gr. at 15.5°	0.9148	0.9145	0.9160	0.9175
Butyro-refractometer reading at 15.5°	67.4	67.4	69.5	66.8
Saponification value	195.7	195.3	197.7	196.2
Iodine value	75.9	77.2	69.7	72.5
Iodine value of { estimated	94.0	....	95.8	93.9
Liquid fatty acids { calculated	98.9	101.3	101.3	97.9
Solid fatty acids, %	18.9	19.3	26.68	21.43
M. p. of mixed fatty acids	33.2°	34.2°	38.4°	35.8°
Free (oleic) acid, %	0.75	0.78	0.28	1.28

Cottonseed oil, unless it has been heated, would be detected by Halphen's colour test; *sesame oil* by the furfural test. Vegetable oils as a class would be detected by the *phytosterol acetate* test. Some vegetable oils would be indicated by the appearance of a well-defined band in the absorption spectrum, near the line B. Genuine lard oil gives no absorption bands.

For the detection of *arachis oil*, Renard's process must be used (see under "Arachis Oil"). Hehner and Mitchell's bromoglyceride test would prove the presence of *fish oils* or *linseed oil*.

The oxidation test described under "Olive Oil" is usefully applied to lard oil intended for lubricating.

NEATSFOOT OIL.

(See also p. 72.) Neatsfoot oil is obtained by boiling the feet of oxen in water until all the oil has risen to the surface. It is usually the custom in rendering establishments to use the whole leg below the knee, and no doubt the majority of the neatsfoot oil of (American) commerce is made in this manner (Lythgoe). The commercial oil also often includes that from the feet of sheep and horses. 10 neatsfoot yield from 2 to 2.5 pints of oil.

Pure neatsfoot oil has a pale golden-yellow colour, a not unpleasant odour of beef fat, and slowly deposits "stearine" on standing. The portion which remains fluid at a low temperature is used as a lubricant for clocks. The commercial oil is largely used for leather dressing and to some extent as a lubricant, chiefly in admixture with mineral oils.

Neatsfoot oil is composed chiefly of olein, with some palmitin and stearin. No ester of a fatty acid less saturated than oleic is present in any quantity (Coste and Shelbourn). The unsaponifiable matter does not exceed 0.7% and consists chiefly of cholesterol and a pigment which tints the oil yellow.

Neatsfoot oil is extensively adulterated with bone oil, fish, seed, and mineral oils. If carefully separated from foreign matters soon after boiling it contains very little free fatty acid, and if preserved under proper conditions very little hydrolysis of the oil occurs. Excessive acidity of the commercial oil must, therefore, be due either to adulteration or to want of proper care in manufacture.

The most complete investigation of this oil has been made by Coste and Shelbourn[1] who prepared a number of samples in the laboratory from the feet of different breeds of oxen and from a calf's feet. A summary of their results is given in the following table, together with some results by other authorities with commercial oils believed to be genuine:

	Coste and Shelbourn. Oil prepared in laboratory	Gill and Rowe. American oil. 5 samples	Lythgoe. American oil. 4 samples	Holde and Stange. 10 genuine oils
Sp. gr. at 15.5°	0.9151–0.9181	0.914–0.919	0.9133–0.9148	.....
Butyro-refractometer, 20°	63.0–64.6	....	63.3–63.6	.....
Saponification value	193.6–199.7	....	....	196–199
Iodine value	66.4–73.1	67.1–72.9	71.3–73.0	66–74
Hehner value	94.8–95.9	....	....	.....
Reichert-Meissl value	0.9–1.2	....	....	.....
Maumené test (100% acid used)	....	42.2°–49.5°	....	.....
Unsaponifiable matter	0.12–0.65	....	....	.....
Mixed Fatty Acids				
Sp. gr. at 100°/100°	0.8713–0.8739	....	....	.....
Titer test	16°–26.5°	....	....	.....
Solidifying-point	24.5–29.2	....	....	.....
Neutralisation value	193.4–206.3	....	....	.....
Iodine value	71.0–77.0	63.6–69.5	....	.....

The *oleo-refractometer* should be of great value in examining samples of neatsfoot oil. The presence of seed oils and fish oils would be readily detected by its means. Sheep's-foot oil is the standard oil used in this instrument.

Observation of sp. gr. and iodine value, together with the Maumené test, would serve to detect many of the most objectionable adulterants. Rape oil would reduce the saponification value. Fish oils and linseed oil would be shown by the bromo-glyceride test. Mineral and rosin oil would be found in the unsaponifiable matter. Bone oil would be detected, most likely, by the ash, and probably would increase the amount of free fatty acid. Vegetable oils, as a class, would be found by the phytosterol acetate test.

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[1] *J. Soc. Chem. Ind.*, 1903, 22, 775.

TALLOW OIL.

(See p. 72.) Tallow oil, or tallow "olein," is obtained by submitting tallow to hydraulic pressure, and its characters differ, as in the case of lard oil, according to the temperature at which it has been expressed. It is largely used as a lubricating oil, especially in admixture with mineral lubricating oils. "Ox" oil should be tallow oil expressed from beef tallow. "Animal" oil might contain the fat of other animals. The name "tallow oil" is sometimes incorrectly applied to crude oleic acid, and care has to be taken that such oil is not inadvertently purchased for lubricating purposes.

Gill and Rowe[1] give analytical constants of 3 samples of tallow oil, as follows:

Sp. gr. at 100°	0.794
Titer test	35° to 37.5°
Maumené test (100% H_2SO_4 used)	35°
Iodine value	55.8 to 56.7
Iodine value of mixed fatty acids	54.6 to 57.0

Two samples of "refined animal oil" examined by Archbutt gave the following numbers:

	1	2
Sp. gr. at 15.5°	0.9187	0.9187
Relative efflux time (seconds) at 15.5° (Refined rape oil, 600–630 seconds)	602	556
Free (oleic) acid	0.20	0.25
Maumené test (97% H_2SO_4 used)	40.5°	42.5°
Saponification value	199.6	193.5
Iodine value	60.4	59.7

On cooling to 50° F., no crystals formed in 3 hours, but on lowering the temperature to 46° F. crystallisation commenced, and slowly continued until the oil ceased to flow.

8 samples of animal oil, believed to be genuine, examined by Dunlop,[2] had iodine values ranging from 66.3 to 77.6 and sp. grs. (15.5°) from

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[1] *J. Amer. Chem. Soc.*, 1902, **24**, 466.
[2] *Analyst*, 1907, **32**, 319.

0.914 to 0.9165. The efflux times of 50 c.c. from Redwood's viscometer at 21.1° ranged from 330 to 460 seconds. Dunlop states that oils of this character are far from common, and that out of more than 40 samples of commercial animal oil tested by him, at least half had a sp. grs. of 0.9170 to 0.9215 and iodine values of 90 to 116. Many of these oils were adulterated with seed or fish oils and had marked drying properties, unfitting them for lubrication; others, of lower sp. gr., were adulterated with mineral oil. The amount of free fatty acid ranged from 0.70 to 22.0%. The Zeiss refractometer is useful as a sorting test, a reading higher than 61 at 25° indicating either a high iodine value or the presence of mineral oil.

Dunlop points out that a high iodine value may be due to the presence of horse oil, four samples of which he prepared from the fat obtained from different parts of the horse. These oils ranged in iodine value from 90 to 115, in sp. gr. at 15.5° from 0.9182 to 0.9212, were lower in viscosity than the genuine animal oils, and had objectionable drying properties. To decide whether a high iodine value is due to the presence of horse oil or a seed oil, the phytosterol acetate test would be necessary.

To test the drying property of tallow oil, Dunlop recommends exposing 2 drops on a 1/4 plate negative glass for 24 hours to a temperature of 95° to 97°. Genuine tallow, lard or neatsfoot oil does not gum to any appreciable extent under these conditions, but many "animal oils" of higher sp. gr. than 0.9170 gave sticky films. Hehner and Mitchell's bromo-glyceride test also gives valuable information, even when used qualitatively, since genuine tallow and lard oils give little or no deposit, while the presence of even 5% of whale or similar oil is indicated by a very distinct precipitate of the bromine compound.

EGG OIL.

This oil, which is used in ointments and cosmetics, also in Russia for cooking, is obtained from the yolk of hard-boiled hens' eggs, either by pressure or by solvents. The yolks contain from 25 to 35% of oil, according to Paladino and Toso.[1] Kitt[2] obtained 19% of oil by extraction with ether.

Egg oil has an orange-yellow colour, is partially solid at ordinary temperatures, gives the Hager-Salkowski indication for cholesterol, and yields a solid elaidin. According to Kitt, the oil is composed chiefly of the ester of oleic acid (82%) with palmitic and stearic acids. It contains cholesterol and lecithin. The results obtained by the above-named chemists are given in the following table:

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[1] *Analyst*, 1896, **21**, 161.
[2] *Chem. Zeit.*, 1897, **21**, 303.

	Paladino and Toso	Kitt
Sp. gr.	0.9156 at 20°	0.9144 at 15°
Solidifying-point	8°–10°	. . . .
M. p.	22°–22.5°	. . . .
Saponification value	185.2–186.7	190.2 (mean)
Iodine value	81.2–81.6	72.1 (mean)
Hehner value	. . . .	95.16
Reichert-Meissl value	. . . .	0.4
Free (oleic) acid	. . . .	0.6
Cholesterol, %	. . . .	1.5
Mixed Fatty Acids.		
M. p.	34.5°–35°	36°–39°
Saponification value	. . . .	194.9 (mean)
Iodine value	. . . .	73.7 (mean)

IX. TALLOW AND BUTTER GROUP.

Beef Fat.
Butter Fat.
Bone Fat.
Horse Fat.
Lard.
Mutton Fat.
Tallow.

BEEF FAT.

(See also p. 72.) Beef fat is more solid than lard, though it differs in consistency as well as in chemical composition with the part of the animal from which it is obtained. It is largely used in the preparation of oleomargarine for the margarine industry, and also as an adulterant of lard (see under "Tallow").

BUTTER FAT.

(See special article.)

BONE FAT. BONE GREASE. BONE TALLOW.

(See p. 72.) Bone fat is obtained by boiling bones with water and skimming the oil; by steaming bones in close digesters; or by extraction with solvents. It is chiefly used for soap- and candle-making.

Bone fat ranges in colour from drab to deep brown, has a characteristic odour, frequently contains a large proportion of free fatty acids, and usually contains lime soaps in solution, besides more or less calcium phosphate, sand, dirt, and water. Its fatty acids usually solidify at about the same temperature as those of lard, though the best samples approach ordinary tallow in this respect. These variations in quality largely depend upon the kind of bones the fat is obtained from, the length of time they have been kept before being treated for the extraction of the fat, the process of extraction employed, etc. Bullocks' hollow shank bones yield the best fat (Carpenter).

In 10 samples of commercial bone fat analysed by Valenta[1] the ash ranged from 0.11 to 2.01%; water from 1.33 to 3.08, except in one very impure, nearly black sample, which contained 6.31%; the total fatty acids ranged from 89.8 to 93.7%; the free fatty acids from 14.8 to 26.5%; the iodine value from 48 to 55.8; the saponification value from 200 to 207; and the m. p. of the fatty acids from 41.5° to 42.7°.

According to Shukoff,[2] the following varieties are recognised in Russian commerce: *Benzine bone fat* (*St. Petersburg*), a very pure fat, containing from 0.65 to 1.0% of water; *benzine bone fat from S. Russia*, usually very impure, containing water and impurities 3 to 4%, free acids 30 to 40%; titer test 40 to 42°; *benzine horse-bone fat*, containing 3 to 4% of water and impurities, titer test 38.2°; *white natural bone fat* (St. Petersburg) from the gelatine factories, containing 0.3 to 1.5% of water and impurities, 20 to 30% of free fatty acids, titer test 40° to 45°.

In 379 samples of bone fat examined by Schestakoff[3] the free fatty acids ranged from 8.3 to 56.2%.

Marrow fat from ox bones, prepared by Dunlop[4] was light yellow, resembled hard lard in consistence, and had the following characteristics: iodine value, 52.04; butyro-refractometer reading at 25°, 55.3; saponification value, 196.3; free fatty acid, 0.22%.

For the valuation of bone fat, Shukoff and Schestakoff recommend the following procedure:[5]

Water.—Dry 5 grm. at 100° to 110° until constant in weight; owing to the tenacity with which the lime soaps retain water, over 24 hours' drying may be required. The water can also be estimated by difference.

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[1] *Zeits. Chem. Ind.*, 1887, 265.

[2] *Chem. Rev. Fett-Harz-Ind.*, 1901, **8**, 229.

[3] *Ibid.*, 1902, **9**, 180.

[4] *Analyst*, 1907, **32**, 318.

[5] *Chem. Rev. Fett-Harz-Ind.*, **5**, 5–8 and 21–23.

Fat, and Non-fatty Impurities.—10 grm. are gently melted on the water-bath, and heated for about an hour with 3 to 5 drops of hydrochloric acid, with frequent stirring, to decompose the lime soaps. The fatty matter is then dissolved out with 40 c.c. of petroleum spirit, which is poured through a tared filter-paper into a weighed flask. The insoluble matter is rinsed on to the filter, well washed with petroleum spirit, dried, and weighed. The fatty matter is estimated by distilling off the solvent and drying at 100 to 110° until constant.

Ash.—This is estimated by careful combustion of a weighed quantity of the fat. The calcium in the ash, existing chiefly as carbonate and oxide, is estimated by titration, and the corresponding amount of lime soaps calculated from the result, 260 being taken as the average molecular weight of the fatty acids. When sand, calcium phosphate, etc., are present, a quantitative analysis of the ash may be necessary, but this is seldom required.

Unsaponifiable Matter.—When the bone fat is intended for soap-making, the unsaponifiable matter should be estimated, as any amount in excess of that natural to the fat, say 2%, must be regarded as an impurity.

Titer Test.—The titer test of the mixed fatty acids is estimated by Dalican's process, as in the case of tallow and other fats.

HORSE FAT.

(See also p. 72.) The fat of the horse is light or dark yellow in colour, and varies in consistency according to the part of the animal it has been obtained from. It consists of the esters of oleic and linoleic acids (the latter constituting about 10% of the total fatty acids), and of saturated fatty acids of which palmitic acid is probably the chief constituent. Horse fat is sometimes used as an adulterant of lard and tallow.

The following results of examination of horse fat and oil have been published by Dunlop:[1]

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[1] *Analyst*, 1907, **32**, 318.

Fat or oil from	Colour and consistence	Sp. gr. at 15.5°	Butyro-refractometer, 25°	Iodine value	Saponification value	Reichert-Wollny value	Unsaponifiable matter, %	Free (oleic) acid, %
1 Belly...........	Orange-yellow, butter-like	......	59.8	85.66	198.4	....	0.54	8.80
2 Neck ("mane")...	Light yellow, part liquid	......	61.2	86.70	199.1	....	....	0.56
3 Neck after filtration at 12.2°....	Lemon-yellow oil	0.9182	61.8	90.10	.....	0.30	0.46	....
4 Neck ("mane")...	Light yellow, part liquid	......	61.2	90.07	.....	....	....	....
5 Neck after filtration at 8.9°.....	Lemon-yellow oil	0.9184	61.8	93.11	195.6	0.20	0.50	1.20
6 Kidney bed.......	Orange-yellow, part liquid	......	66.0	110.65	.....	....	....	....
7 Kidney after filtration at 13.3°....	Orange-yellow oil	0.9212	66.7	114.85	196.3	0.35	0.68	....
8 Oil from neck fat..	Lemon-yellow oil	0.9211	66.0	112.85	196.3	....	0.42	0.46

Dunlop calls attention to the high iodine value, especially of the fat from the kidney bed, which, in the case of most animals, gives a low value. The drying properties of horse fat are very marked, especially at high temperatures. The oils numbered 4 and 5, when exposed to the air in thin films on glass at 95 to 97°, became sticky in two hours, and dried to a varnish in 4 hours. No. 5 sample, tested in Redwood's viscometer, required 286 secs. for the outflow of 50 c.c. at 21.1°. No stearic acid was found in Nos. 1 and 4 samples by Hehner and Mitchell's method.

LARD.

(See special article.)

MUTTON FAT.

(See also page 72.) Mutton fat is, as a rule, more solid than beef fat, but varies in composition and general characteristics according to the part of the sheep from which it is derived (see under "Tallow"). The fat from the region of the kidney, for instance, is hard, while that from the neck is almost fluid. Besides its use as a food, mutton fat is employed in the manufacture of soap, candles, and lubricants. It is also used as an adulterant of lard and butter.

TALLOW.

(See also page 72.) Tallow is the fat of certain ruminant animals, separated from the enveloping membrane of the tissue by the process of melting out or "rendering." Tallow is classed commercially as "beef" and "mutton" tallow, but each of these may comprise the fat of other animals besides the ox and sheep.

Pure tallow is white and almost tasteless, but much of that in commerce has a yellow colour and a disagreeable rancid flavour.

In chemical composition, tallow is composed essentially of the glycerides of palmitic, stearic, and oleic acids, but these do not wholly exist as simple esters, as was formerly believed. Hansen[1] has isolated from beef and mutton tallow palmito-distearin, stearo-dipalmitin, oleo-dipalmitin and oleo-palmito-stearin. On the other hand, Bömer[2] has found about 1 1/2% of tristearin in beef tallow, 4 to 5% in pressed beef tallow, and 3% in mutton tallow. According to Farnsteiner[3] the unsaturated acids include a small amount of linolenic acid. Hehner and Mitchell,[4] in a sample of beef "stearine" of iodine value 2.0, found 50.62% of stearic acid. In several samples of beef tallow, Lewkowitsch[5] found from 21 to 22% of stearic acid. The following table of results by Hehner and Mitchell shows the percentage of stearic acid, etc., found in the fat from different parts of a Scotch sheep 18 months old:

Fat from	Stearic acid in fat, %	Stearic acid in saturated fatty acids, %	Iodine value of fat	M. p. of mixed fatty acids
Kidney	26.2 27.7	58.0	48.16	45.6°
Back	24.8	78.0	61.3	41.4°
Neck	16.4	36.0	48.6	42.2°
Breast	About 1	3.0	58.2	33.8°
Ham	Nil	Nil	50.6	40.8°

The ham fat was fluid, and that from the breast was almost fluid, at the ordinary temperature.

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[1] *Arch. Hyg.*, 1902, **42**, 1.
[2] *Zeitsch. Nahr. Genussm.*, 1907, **14**, 90.
[3] *Ibid.*, 1899, **2**, 1.
[4] *Analyst*, 1896, **21**, 328.
[5] Oils, Fats and Waxes, II, 639.

The following values have been recorded for the fatty acids of tallow (see also page 72):

	Beef tallow	Mutton tallow	Authority
Sp. gr. at 100°/100°	0.8698	....	Archbutt.
Solidifying-point (titer test)	38.3°–46.3°	41.5°–48.3°	Lewkowitsch.
	Usually 43°–45°	Usually 43°–46°	....
Refractive index at 60°	1.4375	1.4374	Thoerner.
Saponification value	197.2–201.6	210	....
Iodine value	26–41	34.8	....
Iodine value of liquid fatty acids	92–93	92.7	Tortelli and Ruggeri; Wallenstein and Finck.

Examination of Commercial Tallow.—The tallow of commerce frequently contains a considerable amount of *free fatty acid.* Thus Deering[1] found in 25 samples of tallow from various sources the proportions of free acid shown in the following table:

Number of samples	Source	Free (oleic) acid, %		
		Highest	Lowest	Average
13	Russian	12.20	2.20	5.48
4	Australian beef	8.85	1.75	4.47
4	Australian mutton	7.15	0.85	3.91
2	Town tallow	6.95	4.55	5.75
1	Unknown	2.10	......	......
1	Town tallow, 6 years old	25.0	......	......

88 samples examined by Archbutt gave the following results:

Number of samples	Source	Free (oleic) acid, %		
		Highest	Lowest	Average
55	Home melted	11.90	1.40	4.89
9	Australian mutton	12.84	1.00	4.84
11	South American beef	7.60	0.70	2.07
12	Unknown	10.60	1.30	4.65
1	Unknown	83.60	....	......

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[1] *J. Soc. Chem. Ind.*, 1884, **3**, 540.

227 samples of tallow, supplied to a specification limiting the free (oleic) acid to 4.0%, contained a minimum of 0.5%, a maximum of 26.2%, and an average of 2.86% of free (oleic) acid.[1]

The free acid in 36 samples of Australian tallow examined by Norman Tate ranged from 1.20 to 4.70, and in 277 samples reported by Schestakoff[2] the free acid found was as follows:

Number of samples	Description	Maximum, %	Minimum, %
158	Mixed tallow..........	56.2	8.3
65	Ox tallow.............	27.0	0.1
54	Mutton tallow.........	10.7	0.33

Large proportions of free acid may be due to adulteration of the tallow with wool-grease acids or stearic acid from cottonseed oil, but they are usually due to hydrolysis of the tallow itself having occurred previous to the rendering of the fat. From whatever cause produced, free acid is objectionable and depreciates the value of the tallow to the candle- and soap-maker, besides unfitting it for use as a lubricant.

Tallow frequently contains more or less water, infusible matters, and mineral impurities, and has been occasionally purposely adulterated with starch, china clay, whiting, barium sulphate, etc. Fats of greater fusibility, especially bone fat, may be present, and wool-grease acids and cottonseed "stearine" have been extensively used. Cakes of tallow are said to have been met with the interior of which consisted of inferior fats.

The presence of *water*, *starch*, and *insoluble substances* generally can be detected and their proportion roughly ascertained by melting a fair sample of the tallow in a graduated cylinder heated in a water-bath, and reading off the volume of impurities which settle out. The insoluble matter in samples of tallow representing large lots is usually under 0.2%, and the water rarely exceeds 1.0 to 1.5%. *Water* can be accurately estimated as described under "Lard." *Insoluble impurities* can be estimated by dissolving 10 to 20 grm. of the tallow in ether or petroleum spirit, filtering through a tared filter-paper, well washing the paper and contents with the solvent to remove fat, drying at 100°, and weighing. The residue on the filter may be examined under the microscope, when *starch*, *gelatinous matter*, or fragments of *tissue* will be readily recognised. Starch may also be detected by boiling the residue with water and testing the solution with iodine. *Lime soap* will be detected by warming the residue with dilute hydrochloric acid, when globules of fatty acids will rise to the top of the liquid, and the latter, after filtration, may be neutralised and tested for calcium with ammonium oxalate. Any effervescence of the residue, on addition of hydrochloric acid, will probably be due to *whiting*.

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[1] Archbutt and Deeley. Lubrication and Lubricants, p. 212.
[2] *Chem. Rev. Fett-Harz-Ind.*, 1902, **9**, 180.

For the detection of foreign fats, paraffin wax, rosin and rosin oil, the quantitative reactions and a few special tests usually suffice.

The *saponification value* of tallow may range from 192.5 to 198, and averages about 195. Paraffin wax would lower this value; palm-nut and coconut oils would raise it. Bone fat, cottonseed oil, and cottonseed "stearine" do not affect this constant.

The *iodine value* of genuine tallow has been found to range from about 33 to 48, but the usual range is from 40 to 45. A value higher than 48.0 would be suspicious, and might be due to the presence of cottonseed oil or "stearine," horse fat, or bone fat. An abnormally low value might indicate paraffin wax, coconut oil, or palm-nut oil.

Smetham[1] has published the iodine values of 1,000 samples of commercial tallow, estimated by Hübl's method. Unfortunately, no attempt was made to discriminate between pure and adulterated samples, but as tallow is not often adulterated, the averages of such a large number of samples cannot be far from the averages of pure tallow of the respective kinds.

Number of samples	Description	Average iodine value
592	Home melted	42.81
46	North American	46.03
5	South American	41.02
62	Australian, unclassified	43.61
69	Australian mutton	42.83
13	Australian beef	45.17
6	Beef	41.42
12	Mutton	41.61
195	Unclassified	43.61

Cottonseed oil and cottonseed "stearine," besides being indicated by the raised iodine value, would probably be detected by Halphen's colour test. The nitric acid test must be used with caution, since it has been observed that tallow which has not been washed and purified and which, therefore, contains particles of blood, etc., acquires a light brown colour when agitated in a melted state with 1/5 of its volume of nitric acid (sp. gr. 1.38). L. Mayer[1] recommends an examination of the "oleine" obtained by allowing the melted tallow to crystallise for 18 hours at 35° and then squeezing the liquid portion through filter cloth. The iodine value of this should not exceed 55 if the tallow be genuine, but in presence of cottonseed oil or stearine a much higher value will be obtained. A more scientific test would be the estimation of the *iodine value of the liquid fatty acids*, those of tallow absorbing 92 to 93% of iodine, while the liquid acids from cottonseed oil absorb nearly 150%. Vegetable oils and fats generally would be detected by the *phytosterol acetate* test (page 301).

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[1] *J. Soc. Chem. Ind.*, 1899, **18**, 330.

Tallow has been occasionally met with which has been largely adulterated with the distilled *fatty acids from wool grease.* Mayer[2] has described a sample which consisted almost exclusively of such fatty acids. It had a very high acid value, smelt strongly of wool grease, yielded only 0.2% of glycerol on saponification, and when the aqueous solution of the soap was shaken with ether and the ethereal solution separated and evaporated, a considerable amount of unsaponifiable matter containing cholesterol was obtained which gave a violet colouration, changing to blue, when evaporated with concentrated hydrochloric acid and ferric chloride. Mayer states that 5% of wool grease can be detected in tallow by this method. The fatty acids separated from the soap formed in the above process turned yellow in a few days, and after several months had acquired a deep orange-yellow tint.

The presence of *bone fat* would be indicated by an excessive amount of *ash*, containing calcium phosphate. In 5 samples of bone fat examined by Valenta the amount of ash ranged from 0.11 to 2.01% averaging 1.32%. Genuine tallow leaves a mere trace of ash. Tallow containing bone fat would most probably be very acid.

Horse fat would tend to make tallow yellow in colour and soft. It would raise the iodine value and would also lower the titer test of the mixed fatty acids. Horse fat contains no stearin. It has marked drying characters, and the intense yellow colour of ethereal solutions of the unsaponifiable matter appear to be characteristic of this fat.[3]

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[1] *Dingl. polyt. J.*, 1883, **247**, 305.
[2] *Loc. cit.*
[3] Dunlop. *Analyst*, 1907, **32**, 317.

Paraffin Wax, which is sometimes added to soft tallow and usually reveals its presence by reducing the saponification value, can be estimated by separating the *unsaponifiable matter*, which, in genuine tallow, does not exceed 0.4 to 0.6%. The same process would indicate the presence of *rosin oil* and also *wool fat.*

Palm-nut and coconut oils, besides raising the saponification value, would increase the *Reichert-Meissl value* and reduce the *Hehner value.*

The varying quality and frequent adulteration of tallow some years since caused the French candle manufacturers to adopt a process of assaying samples for the relative proportions of oleic and solid fatty acids. This they effect by Dalican's method, which consists in estimating the solidifying point of the mixed fatty acids by the "titer test" (see p. 55). The lowest permissible solidifying point of the acids is often fixed at 44°, corresponding to a mixture of oleic and solid fatty acids in equal proportions. The following table by F. Dalican shows the approximate yield of *solid fatty acids* ("stearic acid") from 100 parts of tallow. The corresponding *oleic acid* may be found by subtracting the percentage of solid acids from 95.00.

Solidifying point;°	Solid acids; %	Solidifying point;°	Solid acids; %	Solidifying point;°	Solid acids; %
40.0	35.15	43.5	44.65	47.0	57.95
40.5	36.10	44.0	47.50	47.5	58.90
41.0	38.00	44.5	49.40	48.0	61.75
41.5	38.95	45.0	51.30	48.5	66.50
42.0	39.90	45.5	52.25	49.0	71.25
42.5	42.75	46.0	53.20	49.5	72.20
43.0	43.70	46.5	55.10	50.0	75.05

The titer test of tallow used for making railway wagon axle grease should not fall below 41°.

X. WHALE OIL GROUP.

Codliver and Allied Oils.
Shark-liver Oil.
Menhaden Oil.
Sardine Oil. Japan Fish Oil.
Herring Oil.
Seal Oil.
Whale Oil.
Porpoise Oil.

CODLIVER OIL.

(For constants see p. 73.) Strictly speaking, codliver oil is the oil obtained from the liver of the cod, *Gadus morrhua*, but the closely analogous oils obtained from the livers of other species of *Gadus* and of the Gadidæ family, such as the ling, coalfish, hake, haddock, and whiting, are frequently mixed with codliver oil and cannot in the present state of our knowledge be distinguished from it.

The best Norwegian codliver oil[1] is extracted from the fat livers of the cod caught in the early part of the winter fisheries in the Lofoden Islands. At this season of the year cod is about the only fish caught in that locality, and there is little opportunity of mixing other fish oils with it. The Finmark oil is more liable to be mixed, as the cod caught there are accompanied by large numbers of haddock, ling, and other fish.[2] Newfoundland codliver oil is considered inferior to Norwegian for medicinal purposes, and is sometimes largely adulterated with menhaden and seal oil.[3] Lewkowitsch states that commercial "Coast cod oil" is a liver oil which may have been obtained from any fish which the trawlers' nets bring up from the open sea; it may, therefore, contain oil from the shark, dogfish, etc., in addition to those mentioned in the first paragraph.

Several qualities of codliver oil are recognised in commerce: pale, used only in medicine; light brown, an after-yield, of inferior quality, but still largely used in medicine; and dark brown, or tanners' oil, obtained by roughly boiling down the livers remaining from the foregoing processes.

The purest codliver oil has a pale yellow colour, and is never quite colourless unless artificially bleached. It is limpid, has a slight odour and taste, and a faint acid reaction. If prepared at a high temperature, or if the livers be allowed to partially putrefy, the acid reaction is more decided and the colour pale or dark brown, the darkest varieties being transparent only in thin layers, and having a repulsive, fishy odour, and bitterish, acid taste.

The composition of codliver oil is very complex and not yet fully known. By fractionating the methyl esters of the fatty acids in vacuo, Bull[4] found that about 80% distilled over below 240°, and from these he obtained the saturated acids, myristic and palmitic, with a small quantity of stearic acid, the unsaturated acids, oleic and erucic, and two new acids, to one of which he gave the formula $C_{16}H_{30}O_2$, and to the other $C_{20}H_{38}O_2$. The latter he named *gadolinic acid;* it is said to occur in large quantity. By the sodium-salt-ether method Bull has also isolated from Norwegian codliver oil from 17 to 21% of highly unsaturated acids, absorbing from 306 to 324% of iodine, which he states belong mainly to the series $C_nH_{2n-8}O_2$. (See also under "Sardine Oil.") These various acids exist as glycerides. Allen observed the presence of a sensible quantity of cholesterol and of volatile fatty acids. The latter, however, appear to be secondary products, due to putrefactive changes in the livers, and are not met with in medicinal codliver oil.

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[1] *U. S. Consular Report* No. 1843, Jan. 6, 1904.
[2] Mann. *Pharm. Jour.*, 1903, **71**, 840.
[3] Sage. *Chemist and Druggist*, 1903, **62**, 571.
[4] *Chem. Zeit.*, 1899, **23**, (2), 996 and 1043. *Berichte*, 1906, **39**, 3570.

The following bases have been isolated from codliver oil: butylamine, isoamylamine, hexylamine, dehydrolutidine, morrhuine, and aselline. Trimethylamine, derived probably from the decomposition of the liver tissue, has also been detected.

The presence of biliary compounds, as stated by earlier investigators, is now denied.

Codliver oil contains traces of iodine and sometimes of bromine, but the form in which these elements exists is unknown. The proportion of iodine, judging from the statements of different investigators, is variable. The question has been reinvestigated by E. C. Stanford, who found the proportion of iodine to be extremely minute, ranging from 0.138 to 0.434 mg. per 100 grm., with an average of 0.322. The proportion in the flesh of dry cod-fish and herrings is considerably larger than in codliver oil.

The mixed fatty acids of codliver oil have been found to possess the following characters:

		Authority
Refractive index at 60° F.	1.4521	Thoerner.
Solidifying-point (titer test)		
Norwegian oil	13.3°–13.9°	Lewkowitsch.
Medicinal oil	17.5°–18.4°	Lewkowitsch.
Coast cod oil	18.7°–19.3°	Lewkowitsch.
Dark unracked oil	22.5°–24.3°	Lewkowitsch.
Iodine value	164–171	Parry.
Mean molecular weight	287–290	Parry.

Examination of Codliver Oil.—Codliver oil to which iodine or compounds of iodine have been purposely added is employed in medicine. These additions are dissolved on agitating the oil with alcohol, and can be detected in the spirituous solution by the usual tests. The ash left on igniting natural codliver oil contains no trace of iodine, but if an iodide has been added it will be found in the incombustible residue. The usual proportion of iodine in iodised codliver oil is about 0.1%.

A ferrated codliver oil is also employed, containing about 1% of ferrous oleate.

Good *medicinal codliver oil* should deposit no solid fat at 0° (*Pharm. Germ.*), but a granular crystalline deposit is often produced on cooling oils of the lower qualities.

The *British Pharmacopœia* describes codliver oil as pale yellow, with a slight fishy, but not rancid odour. It states that it is the oil extracted from the fresh liver of the cod, *Gadus morrhua*, by the application of a temperature not exceeding 180° F. (82.2°); and from which solid fat has been separated by filtration at about 23° F. (−5°). It states that no solid fat should separate on exposure of the oil for 2 hours to a temperature of 32° F. (0°), but no test is given by which the oil from *Gadus morrhua* can be distinguished from allied oils.[1]

As previously stated, the "codliver oil" of commerce is in practice obtained from several members of the *Gadidæ*, or cod family; and, as long as it is produced from these fish solely, little exception can be taken. The livers of various other fish are, however, apt to be employed, and the detection of the substitution is very difficult. Adulteration with fish oils, such as menhaden oil, with blubber oils, such as porpoise, seal, and whale oils, and with mineral and rosin oils is also practised.

The constants of a number of fish-liver oils other than codliver oil, many of which were prepared from the fresh livers by Thomson and Dunlop and were, therefore, undoubtedly genuine, are given in the table on page 221. Thomson and Dunlop,[2] who have studied the question carefully, are of opinion that, so far as present knowledge goes, taking into consideration the wide limits of variation of cod oils and the small amount of information we possess of the others, coalfish, haddock, hake, ling, whiting, and skate liver oils are practically undistinguishable from each other and from codliver oil by chemical or physical tests. They also believe the detection of seal oil to be almost impossible by chemical methods, and whale oil difficult. The smaller yield of brominated glycerides, however, enables seal and whale oils to be detected and may eventually be found useful in detecting some of the others, such as coalfish oil. The liver oils, such as shark and dogfish, which contain large amounts of unsaponifiable matter may be detected by means of this characteristic, if present in sufficient proportion, and porpoise oil can be easily detected, even in small proportion, by means of its high saponification and Reichert values.

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[1] The United States Pharmacopœia describes codliver oil as "a fixed oil, obtained from the fresh liver of *Gadus morrhua* Zinni, and of other species of Gadus."

[2] Papers read before the Association of Public Analysts of Scotland, June, 1905, and Jan., 1906.

The *sp. gr.* of codliver oil ranges from about 0.922 to 0.930 at 15.5°, the darker varieties being generally the heavier. The United States Pharmacopœia demands a sp. gr. of 0.918 to 0.922 at 25°, which corresponds with about 0.923 to 0.927 at 15.5°. The oil from fish allied to the cod is sometimes of a slightly higher sp. gr. Thus, that prepared in Grimsby from a mixture of the livers of cod, haddock, ling, and whiting has a sp. gr. of 0.930; while the product obtained in Aberdeen from haddock livers has a sp. gr. of 0.931, is somewhat less viscous, and develops more heat with sulphuric acid than the other varieties of codliver oil. A sample of very much decomposed (44% free acid) brown codliver oil examined by Bull had a sp. gr. of 0.941. It is evident that the sp. gr. affords no reliable indication of the presence of other fish oils in codliver oil.

The *iodine value* (Wijs) usually ranges from about 154 to 170, but a value as high as 181 has been recorded (Wijs). With reference to some of the very low numbers, below 154, which have been published, it may be noted that values estimated by the Hübl method are from 6 to 10% lower than those by the Wijs method for this oil, also that the oil from decomposed livers is lower in iodine value than that from fresh livers.

The *saponification value* ranges from about 179 to 190. A lower value might be due to shark liver or dogfish liver oil, if accompanied by an excessive amount of the kind of unsaponifiable matter characteristic of those oils, or it might indicate the presence or rosin or mineral oil, which would be found wholly in the unsaponifiable matter. An abnormally high value might be due to porpoise oil.

The *refractometer* is of limited use, except as a rapid sorting test, and in this respect it is inferior to the iodine value. Dowzard[1] found the refraction of 13 samples of Newfoundland and Norwegian and 1 sample of English codliver oil to range from +43.5 to +45.0 when tested in Amagat and Jean's *oleo-refractometer* at 22°, while 3 samples of pale seal oil ranged from +32.0 to +32.5, and he gave a table showing that

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[1] *Pharm. J.*, 1898, 532.

20% and upwards of seal oil could be detected by this instrument. But Pearmain's numbers (+40 to +46 for codliver oil and +30 to +36 for seal oil) show a much wider range for each oil and a much smaller difference between the two oils. Further tests of authentic samples with this refractometer seem desirable. Utz[1] states that Newfoundland and Norwegian oils can be distinguished by means of the butyro-refractometer, and gives the following values. For comparison, results by Lythgoe,[2] Liverseege,[3] and Thomson and Dunlop are also given.

Description of oil	Newfoundland		Norwegian		West coast	East coast	Unknown	Unknown
Observer	Utz	Liverseege	Utz	Liverseege	Thomson and Dunlop			Lythgoe
15°	80.8–81.5	....	82.0–86.7	....	.....	.....	....	82.5–85.1
20°	77.5–78.1	....	78.6–83.2	....	.....	.....	....	79.3–81.9
25°	....	76.3–79.0	....	79.7–80.0	75.7	78.0	76.0–76.5	76.2–78.8
40°	....	....	....	....	66.7	69.0	67.0–67.5	....

The *Reichert-Meissl* value of genuine codliver oil should not exceed about 0.4. A higher number would indicate that the oil had been prepared from livers which had undergone putrefaction, and in this case the iodine value would be lower and the sp. gr. higher. In illustration of this, Thomson and Dunlop give the following results:

EFFECT OF OXIDATION ON CODLIVER OIL.

	Sample A		Sample B	
	Fresh	After oxidation	Fresh	After oxidation
Sp. gr. at 15°	0.9263	0.9321	0.9248	0.9378
Butyro-refractometer at 25°	78.0	79.0	75.7	77.3
Iodine value (Wijs)	167.3	164.2	153.7	143.4
Saponification value	187.9	190.7	186.0	197.0
Reichert-Wollny value	0.4	1.4	0.5	3.3
Free (oleic) acid	1.20	3.01	0.20	2.25

An abnormally high value might be due to the presence of porpoise oil, which has such a high Reichert value that a very small quantity would betray its presence.

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[1] *Zeits. öffentl. Chem.*, **8**, 304.
[2] *J. Amer. Chem. Soc.*, 1905, **27**, 887.
[3] *Analyst*, 1904, **29**, 210.

The *unsaponifiable matter* in genuine codliver oil contains cholesterol, and does not exceed 1.5%. A higher percentage would indicate the presence of shark-liver oil, dogfish, sunfish, mineral, or rosin oil. The presence of phytosterol would prove the presence of vegetable oil.

Free fatty acid in fresh codliver oil should be very trifling in amount; medicinal oil should not contain more than 1 to 1.5% as a maximum; but in dark coloured, partially decomposed oils the acids may amount to 20 or 30% or even more.

The *yield of insoluble brominated glycerides* from some fish oils, notably seal oil, is much lower than from codliver oil and is the most characteristic test yet discovered for the detection of these oils. In the following table, some results by Hehner and Mitchell, Walker and Warburton, and Lewkowitsch are summarised in the first column, and in the second Procter and Bennett's "Bromide Values" are given. These figures show the possibilities of the methods and the desirability of collecting further data:

Kind of oil	Percentage yield of brominated glyceride by Hehner and Mitchell's method	"Bromide value" (Procter and Bennett)
Codliver, brown	....	60.4
Codliver, undescribed	34.5–42.9	....
Codliver, Newfoundland	31.6	49.0
Codliver, Möller's	....	42.1
Menhaden	....	53.3–59.9
Fresh herring	....	44.8
Whale	15.7–25.0	27.3–37.4
Coalfish	....	29.8
Seal	....	13.9–14.1
Shark-liver	20.2–22.0	16.5
Japan fish	21.6	....
Linseed	23.1–37.7	24.8

As most vegetable oils other than linseed yield no bromoglycerides, or only very small amounts, a low yield might be due to the presence of a vegetable oil. The phytosterol acetate test would decide the question.

The British Pharmacopœia gives the following colour test:

"A drop of sulphuric acid added to a few drops of the oil on a porcelain slab develops a violet colouration."

In the United States Pharmacopœia the following three tests are given:

1. "If 1 drop of the oil be dissolved in 20 drops of chloroform and the solution shaken with 1 drop of sulphuric acid, the solution will acquire a violet-red tint, rapidly changing to rose-red and, finally, brownish-yellow." (In the German Pharmacopœia the oil is directed to be dissolved in carbon disulphide instead of chloroform.)

2. "If a glass rod moistened with sulphuric acid be drawn through a few drops of the oil on a porcelain plate, a violet colour will be produced."

3. "If 2 or 3 drops of fuming nitric acid be allowed to flow alongside of 10 or 15 drops of the oil, contained in a watch-glass, a red colour will be produced at the point of contact. On stirring the mixture with a glass rod, the colour becomes bright rose-red, soon changing to lemon-yellow (distinction from *seal oil*, which shows at first no change of colour, and from *other fish oils*, which become at first blue and afterwards brown and yellow)."

In regard to the above tests, it may be remarked that the violet colouration produced by sulphuric acid is characteristic, not of codliver oil alone, but of liver oils generally. Rancid oils do not give the violet colour, but only the red. Thomson and Dunlop have obtained the violet colour with porpoise and seal oils which they extracted themselves from the blubbers and, therefore, the test is not exclusively characteristic even of liver oils. It is, in fact, really of very little use, and, as Lewkowitsch has pointed out, it depends entirely upon the presence in the oil of impurities which the modern processes of extraction and refining tend to eliminate, so that the purer the oil the less marked the indication becomes. As regards the test with fuming nitric acid, Tolman has shown that it is liable to give misleading results with perfectly genuine codliver oils of American origin. A variety of other colour tests have been proposed, but as they are more likely to mislead than to afford reliable information respecting the genuineness of codliver oil it is not thought worth while to describe them.

Skate-liver oil, obtained from *Raia batis*, has been proposed as a substitute for codliver oil. It is bright or golden yellow in colour, is neutral in indication, and has a slightly fishy odour and taste. It darkens but little under the influence of chlorine, and is said to give an odour of valeric acid when heated with a solution of alkali. A sample examined by Thomson and Dunlop gave the results shown in the table on p. 221.

SOME FISH-LIVER OILS OTHER THAN CODLIVER.

Kind of oil	Brusmer	Coalfish			Haddock		Hake	Hoi	Ling			Skate	Whiting
Authority	Liverseege	Bull	Bull	Thomson and Dunlop	Liverseege	Thomson and Dunlop	Thomson and Dunlop	Liverseege	Bull	Liverseege	Thomson and Dunlop	Thomson and Dunlop	Thomson and Dunlop
Particulars of source	Norwegian	Aalesund, clear	Aalesund, clear	Prepared in laboratory from the fresh liver	....	Prepared in laboratory from the fresh liver	Prepared in laboratory from the fresh liver	Norwegian	Aalesund, clear	....	Prepared in laboratory from the fresh liver	Prepared in laboratory from the fresh liver	Prepared in laboratory from the fresh liver
Sp. gr. at 15°	....	0.9268	0.9254	0.9261	....	0.929	0.9256	....	0.9200	....	0.924	0.9298	0.929
Sp. gr. at 15.5°	0.923	....	....	....	0.934	....	....	0.919	....	0.923	....	....	....
Butyro-refractometer at 25°	75.0	....	....	77.0	84.0	81.0	76.0	73.7	....	74.0	75.0	82.5	81.0
Butyro-refractometer at 40°	66.3	....	....	....	74.3	72.0	....	64.7	....	65.0	....	73.5	72.0
Valenta test, °[1]	108°	....	....	....	73°	....	....	113°	....	105°	....	....	....
Free (oleic) acid, %	0.05	3.6	10.9	0.27	0.3	2.37	1.05	0.05	5.5	0.05	0.34	0.33	0.65
Unsaponifiable matter, %	....	....	1.83	1.14	1.0	1.30	1.38	....	2.23	....	1.0	1.08	1.06
Iodine value.[2]	138 H	162.2	....	161.1 W	179 H	186.4 W	154.0 W	124 H	132.6	133 H	151.8 W	191.1 W	....
Saponification value	183	183.7	186.2	187.2	193	187.2	190.7	169	184.1	188	187.2	187.9	187.9
Specific temperature reaction	....	....	....	257	....	300	....	....	....	......	232	322	317
								If this is the piked dogfish as suggested by Prof. Bridge, it belongs to the shark-liver oils.					

[1] The acid used gave 65° with butter fat, and 94°–96° with codliver oil.

[2] H = Hübl.
W = Wijs.

SHARK-LIVER OIL. SHARK OIL.

(See also pages 73 and 223.) The shark oil known in commerce is chiefly obtained from the liver of the basking shark (*Cetorhinus* (*Selache*) *maximus*), chiefly caught off the coast of Norway, but the dogfish and several allied fish also contribute to it.

Shark oil has been largely employed in tanneries and as a substitute for codliver oil, but in England it is now almost disused.

Owing to frequent adulteration, the physical and chemical characters of shark oil have been misstated by many authorities. Thus it has been alleged to be of very low sp. gr., a character in all probability really due to the presence of a large proportion of mineral oil or similar adulterant. Whether or not these oils of low sp. gr. were uniformly adulterated is no longer of practical interest, as oil of such character is not now met with. The "shark oil" usually indicated 40° to 42° on Casartelli's oleometer, and the analogous "African fish oil" 48° to 50° (see foot-note, page 233).

Shark oil is peculiar in yielding a very notable proportion of unsaponifiable matter, consisting in great part of cholesterol. If the sample be saponified in the usual way, and the aqueous solution of the soap agitated with ether, the separated ethereal layer leaves on evaporation a nearly colourless crystalline mass, which, if dissolved in boiling alcohol, deposits abundant plates of cholesterol, which yield the characteristic colour-reactions.

Analyses of a number of shark-liver and some other oils are given in the following table. It will be noticed that the percentage of unsaponifiable matter is irregular.

Shark oil has been found to yield from 20 to 22% of an insoluble brominated ester by Hehner and Mitchell's process, and the "bromide value" of a specimen examined by Procter and Bennett was found to be 16.5—much lower than that of codliver oil.

In regard to the three last-named oils in the following table, the "dogfish" is probably *Acanthias vulgaris*, the piked dogfish, a small shark frequently seen in shoal water on British coasts. The "crampfish" may be one of the electric rays, *Torpedo*. The "sunfish" may be the basking shark, which floats with its dorsal fin above the water like the true sunfish, *Orthagoriscus mola;* the latter is not a shark.

ANALYSES OF SHARK OIL, ETC.

Authority	Description	Sp. gr.		Butyro-refractometer, 25°	Unsaponifiable matter, %	Free (oleic) acid, %	Iodine value	Saponification value	Hehner value	Acetyl value
		15°	15.5°							
Allen	Japanese		0.9260		2.82			177.3		
Allen	Crude		0.9185		8.70			169.6		
Allen	Refined		0.9285		0.70			197.6		
Allen			0.9143		10.25			153.0		
Allen			0.9136		17.30			140.0		
Allen			0.9113		10.34			140.0		
Bull	Norwegian (Finmark)	0.9105			21.18	3.1	111.9	146.1		
Bull	Norwegian (Finmark)	0.9130			21.08	1.3	114.9	148.5		
Bull	Japanese	0.9156			14.39	0.75	128.3	163.4		
Bull	Japanese	0.9177			12.54	0.44	136.0	163.5		
Bull	Dark Japanese	0.9166			2.43	19.9	116.3	183.2		
Lewkowitsch	Arctic	0.9163			10.2		114.6	161.0	86.9	11.9
Thomson and Dunlop				72.0	15.28					
Thomson and Dunlop	Dogfish oil, prepared in laboratory from the fresh liver	0.9179		71.2	8.40	trace	126.4	169.7		
Bull	Crampfish oil, American	0.9090			21.97	0.39	107.3	148.2		
Bull	Sunfish oil, American	0.901			24.12	1.07	102.7	147.6		

MENHADEN OIL.

(See p. 73.) This oil is obtained from *Alosa menhaden*, a North American fish allied to the herring. It is derived from the whole body of the fish, by boiling with water and pressing. It resembles codliver oil in many respects, and is used to adulterate Newfoundland codliver oil (Sage). It is chiefly employed for dégras and as a currying oil. Sometimes it is added as an adulterant to linseed oil. Some constants and variables of menhaden oil are given in the following table:

Authority	Thomson and Ballantyne	Bull		Liverseege
Description	Brown	Extra refined	Natural pressed	
Sp. gr. at 15°	....	0.9311	0.9284	....
Sp. gr. at 15.5°	0.9311	....	....	0.931
Butyro-refractometer, 25°	....	....	....	80.7
Butyro-refractometer, 40°	....	....	....	71.3
[1]Valenta test, °	....	....	....	78°
Free (oleic) acid, %	7.57	nil	5.4	0.25
Unsaponifiable matter, %	1.60	1.43	2.15	0.6
Iodine value (Hübl)	160.0	172.6	139.2	174.0
Saponification value	189.3	188.75	193.0	193.0

Adulteration with mineral or rosin oil would be detected by estimating the unsaponifiable matter, which in genuine menhaden oil does not exceed about 2%.

SARDINE OIL. JAPAN FISH OIL.

(See p. 73.) Sardine oil is obtained from species of sardines belonging to the family *Clupeidæ*. According to a recent paper by Tsujimoto,[2] Japanese sardine oil is obtained from *Clupanodon melanosticta* T. and S., and does not possess the low iodine value commonly attributed to it. Three authentic samples examined by him had (Wijs) iodine values of 180.7, 180.6, and 187.3, respectively (see table below). These samples were greenish-brown to reddish-brown in colour, and all deposited large quantities of "stearine" at low temperatures. The iodine values of the samples examined by Bull were probably estimated by the Hübl method, and one, at any rate, of the samples (the last), besides being a badly decomposed oil, was of very suspicious quality.

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[1] The acid used gave 65° with butter fat, and 94° to 96° with codliver oil.

[2] *J. College of Engineering*, Tokyo Imp. University, 1906, 4, 1.

Tsujimoto obtained from the mixed fatty acids 44.2 to 47.1% of an insoluble octobromide derived from an acid of the formula $C_{18}H_{28}O_2$, belonging to the series $C_nH_{2n-8}O_2$, to which he gave the name of *clupanodonic acid*, and states that it constitutes about 13 to 14% of the mixed fatty acids from the oil. The free acid liberated from the bromide was a pale yellow liquid of a fishy smell, which oxidised in the air and formed a dry varnish. Iodine value, 344.4. No insoluble hexabromide was obtained. The same acid was found in herring oil (3.8 to 6.5%) and in whale oil (8.39%). Bull[1] had previously assumed the existence of highly unsaturated acids of the $C_nH_{2n-8}O_2$ and $C_nH_{2n-10}O_2$ series in fish oils, and had isolated from a large number of different kinds of oil by the sodium-salt-ether method variable percentages of acids absorbing more than 300% of iodine. A sample of Japan fish oil examined by Walker and Warburton[2] gave 21.6% of an insoluble bromo-glyceride, and the mixed fatty acids from the same sample gave 23.2% of an insoluble bromide by Hehner and Mitchell's process.

The Japanese sardine oil of commerce is obtained by boiling with water and pressing the entire fish. It is liable to be mixed with other fish oils. It is principally used in commerce for making soap and dégras.

Authority	Source and description	Sp. gr.		Refractive index, 20°	Unsaponifiable matter. %	Free (oleic) acid, %	Iodine value W = Wijs	Saponification value	M. p. of mixed fatty acids
		15°	15.5°						
Bull	Japan, clear	0.9283	......	......	1.96	1.1	134.1	189.0	......
Bull	Japan, white ...	0.9338	......	......	1.55	1.1	162.4	193.7	......
Bull	Japan, white ...	0.9279	......	......	1.9	6.0	156.2	191.9	......
Bull	Japan, white ...	0.9272	......	......	1.81	7.2	138.3	191.4	......
Bull	Japan pale brown	0.9324	......	......	0.95	6.9	171.3	190.6	......
Bull	Japan, turbid...	0.9155	......	......	2.27	17.3	104.0	178.8	......
Tsujimoto	Chita	......	0.9347	1.4808	......	0.66	180.7W	195.8	35.4°
Tsujimoto	Chōshi	......	0.9318	1.4802	......	4.11	180.6W	196.2	36.2°
Tsujimoto	Hakodaté	......	0.9316	1.4807	......	2.58	187.3W	194.8	35.8°

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[1] *Chem. Zeit.*, 1899, **23**, 1044.
[2] *Analyst*, 1902, **27**, 937.

HERRING AND OTHER FISH OILS.

The following characteristics of commercial herring oil have been published by Bull. Figures obtained with sturgeon oil and "whitefish" oil are added.

Kind of oil	Sp. gr. 15°	Free (oleic) acid, %	Unsaponifiable matter, %	Iodine value	Saponification value
Herring oil, white, Japanese	0.9215	0.9	10.68	131.0	170.9
Herring oil, white, Japanese	0.9222	4.1	7.75	141.4	175.9
Herring oil, clear, Japanese	0.9254	5.4	1.58	142.0	188.3
Herring oil, clear, Japanese	0.9310	7.9	2.15	131.8	193.7
Herring oil, turbid, Japanese	0.9202	6.0	1.33	134.2	184.6
Herring oil, cold-filtered, Japanese	0.9202	7.3	1.39	135.5	184.7
Herring oil, brown, English	0.9391	20.2	2.64	132.7	184.8
Sturgeon oil, American	0.9236	0.11	1.78	125.3	186.3
Whitefish oil, Finmark	0.9268	2.0	1.75	127.4	201.6

SEAL OIL.

(For constants see page 73.) This oil is rendered in Greenland from the blubber of different species of seal, *Phoca greenlandia*, etc., and is subsequently refined in Denmark. Chemically it is composed of glycerides of saturated fatty acids (palmitic acid) and unsaturated fatty acids, including oleic and physetoleic acids (Ljubarsky). Linolic and still more unsaturated fatty acids have also been found in seal oil. Thus, Bull obtained from 2 samples 7.78 and 11.96% of highly unsaturated acids absorbing, respectively, 306.1 and 330.3% of iodine. Procter and Bennett obtained a much smaller yield of brominated esters from seal oil than from codliver oil (see under "Codliver Oil").

Commercial seal oil varies in colour from very pale yellow ("Water White") to dark brown, and from the figures which have been published by several observers it appears to be very uniform in character. Thus, the published sp. gr. numbers at 15° to 15.5° range between the narrow limits of 0.9238 to 0.9267, and the iodine values estimated by the Hübl method between 132 and 152. A sample rendered in the laboratory by Thomson and Dunlop had a Wijs iodine value of 162.6. The published saponification values range from 187.5 (Bull, Sandefjord oil) to 191.4 and the percentages of unsaponifiable matter from

0.38 to 1.00, except that in the Sandefjord sample of low saponification value Bull found 1.8% of unsaponifiable matter.

Seal oil readily oxidises and is unsuitable for use as a lubricant. It evolves rather less heat with sulphuric acid than codliver oil. At 15.5° it has about 3/5 of the viscosity of refined rape oil. In the butyro-refractometer the following readings have been obtained:

	25°	40°
Liverseege	72.7	64.0
Thomson and Dunlop, Commercial oil	73	64
Thomson and Dunlop, oil rendered in laboratory	76.2	......

2 samples of oil from the Vikare seal, *Phoca fœtida*, examined by Schneider and Blumenfeld[1] had distinctly higher sp. gr. and iodine values than the ordinary commercial oil, as is shown below:

	Oil from Phoca fœtida	
Sp. gr. at 15°	0.9321	0.9336
Butyro-refractometer, 20°	87	....
Free (oleic) acid, %	0.24	0.54
Iodine value (Hübl)	191.3	193.3
Saponification value	188.5	189.0
Hehner value	95.6	95.8
Reichert-Meissl value	1.55	0.96
Mixed Fatty Acids.		
Solidifying-point	13.0°	14.0°
Iodine value	195.3	201.8
Neutralisation value	196	198

WHALE OIL (TRAIN OIL).

(See p. 73.) Whale oil proper is from the blubber of the Greenland or Arctic "right" whale, *Balæna mysticetus;* but commercial whale oil includes the oil from the southern right whale, *Balæna australis*, and other species of *Balænidæ* and *Balænopteridæ* (fin-backed whales) belonging to the sub-order *Mystacoceti*, or whalebone-yielding whales. The term "train oil," formerly applied to whale oil, is now extended to the oil from the blubber of any marine animals, including seals.

The oils from the different species of dolphin and porpoise (*Delphin-*

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[1] *Chem. Zeit.*, 1905, 29, 53.

idæ) are glyceridic in nature, like ordinary whale oil, but the oils from the Cachalot and probably other toothed cetaceans are essentially different both in chemical constitution and practical applications, and hence are described in another section (see page 232).

Whale oil is usually extracted by boiling the blubber with water and skimming the oil from the aqueous liquid and refuse tissue. It is graded according to colour, taste, smell, and acidity; the highest grades being pale coloured, nearly neutral oils, of only slight odour, and the lower grades dark coloured, acid oils, having a marked and offensive "fishy" smell and taste. In the United States crude whale oil is separated by refrigeration and pressing into "winter whale oil," congealing at 36° to 40° F. and "whale foots" or "stearine." Occasionally "spring" and "summer" oils are also produced. By the usual method of pressing, the oil of the "right" whale, taken in high northern latitudes, gives about 8% of "stearine"; that of the whales taken in the vicinity of the equator or south of it, about 15%; humpback or finback whales give 12% (*United States Fish Commission Report*, 1902). The whale oil "stearine," which consists largely of palmitin, is sometimes used for soap-making, though the odour of the product indicates its origin. The oil from the finback whales is considered inferior to that from the "right" whales; some varieties, especially the southern product known in commerce as Bahie whale oil, exhibit strongly marked drying properties. The results of examination of a number of commercial whale oils by Bull[1] are given in the following table:

Description	Sp. gr. at 15°	Free (oleic) acid, %	Unsaponifiable matter, %	Iodine value	Saponification value
Arctic whale oil, refined, American....	0.9234	0.95	2.11	117.4	185.0
Antarctic "right" whale oil, American.	0.9257	0.28	1.46	136.0	183.1
Crude white whale oil, American	0.9222	1.25	1.37	127.4	183.9
Whale oil No. 1, unrefined, Finmark ..	0.9181	0.43	2.36	104.0	188.6
Whale oil No. 2, unrefined, Finmark ..	0.9182	1.8	3.3	....	188.3
Whale oil No. 3, unrefined, Finmark ..	0.9162	13.3	2.42	96.0	185.7
Whale oil No. 4, unrefined, Finmark ..	0.9205	29.1	3.4	89.0	182.1
Whale oil No. 1, refined, Glasgow	0.9214	0.7	2.33	113.2	184.7
Yellow whale oil, refined, Glasgow....	0.9232	5.3	1.89	110.0	185.9
Brown whale oil, refined, Glasgow....	0.9272	18.6	3.22	125.3	160.0
Dark whale oil, refined, Glasgow	0.9170	49.3	3.03	103.1	178.3

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[1] *Chem. Zeit.*, 1899, 23 (2), 1044.

The chemical composition of whale oil is variable. It is composed of esters of saturated and unsaturated acids, some of the latter being highly unsaturated. Hehner and Mitchell obtained 25%, and Walker and Warburton a mean of 15.84% of brominated ester from 2 samples. Bull, by the sodium-salt-ether method, found a smaller proportion of highly unsaturated acids in whale oil than in most other marine oils. Tsujimoto found 8.39% of an acid of the $C_nH_{2n-8}O_2$ series (see under "Sardine Oil").

The amount of unsaponifiable matter is variable, but does not exceed 4%. This and the much higher sp. gr. readily distinguish ordinary whale oil from the sperm oils. Adulteration with mineral or rosin oil would, of course, increase the percentage of unsaponifiable matter. Rosin oil is the most likely adulterant. A sample of "whale oil" supplied for oil-tempering steel, examined by the reviser, had a sp. gr. of 0.9608 at 15.5°, required only 7.72% of potash for saponification, and contained 60.3% of unsaponifiable matter of sp. gr. 0.981, easily soluble in acetone.

The recorded sp. grs. of genuine whale oil range from 0.917 (Liverseege) to 0.927 (Bull); the saponification values from 188 to 194 (Schweitzer and Lungwitz), the low value of 160 obtained by Bull being exceptional. The range of iodine values is wide, 89 to 136 in the samples examined by Bull, and there was also a fairly wide range in the percentages of highly unsaturated acids which he found by the sodium-salt-ether method.

8 samples of whale oil examined by Milrath[1] in the butyro-refractometer gave readings of 63.1 to 70.2 at 25° and 56.2 to 63.0 at 40°.

The mixed fatty acids of whale oil have been found to possess the following characteristics:

		Authority
Sp. Gr. at $\frac{100°}{100°}$	0.8922	Archbutt.
Solidifying-point (titer test)	22.9°–23.9°	Lewkowitsch.
Butyro-refractometer reading, 40°	43.3	Liverseege.
Iodine value	130.3–132.0	Schweitzer and Lungwitz.

Whale oil is liable to adulteration with seal oil, which so nearly resembles whale oil that it cannot be detected by chemical means, except perhaps by a lowering of the "bromide value" (see under "Codliver oil").

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[1] *Zeitsch. öffentl. Chem.*, 1907, **19**, 371.

Whale oil is used as an illuminant and to some extent as a lubricant. The lower grades are used in leather manufacture and for tempering steel.

PORPOISE OIL.

(See also p. 73.) Commercial porpoise oil is derived not only from the black porpoise, *Phocœna communis*, usually caught off the coast of Denmark and in the Mediterranean and Black Sea near Trebizond, but also largely from the beluga or white whale, *Delphinapterus leucas*, caught in the White Sea, the St. Lawrence, and on various parts of the Canadian coasts. The oils from the "grampus" or killer whale, *Orca gladiator*, and the various species known as blackfish, especially *Globicephalus melas*, also rank as "porpoise oil."

Porpoise oil is prepared in much the same manner as whale oil. In some instances, oil of a superior quality drains from the blubber at the ordinary temperature, but the greater part is obtained by boiling the tissue with water. The oil is pale yellow to brown in colour and, according to Schaedler, is composed of the glycerides of valeric, palmitic, stearic, physetoleic, and oleic acids.

The liquid "oleine" obtained from the soft fat of the head and jaw by exposing the fat to a low temperature and straining off the oil which remains fluid, contains a much larger percentage of valerin and of unsaponifiable matter than the body oil. In the case of *G. melas*, the mass of fat taken from the head has the shape of a half watermelon, and the liquid oil obtained from it is known as "melon oil." These jaw oils are specially prepared in America for lubricating watches and other delicate mechanisms, and command a high price. The body oils are also used for lubricating.

Porpoise oil is remarkable for the large proportion of valerin which it contains. A sample examined by Allen yielded 5.06% of volatile fatty acids, having a mean combining weight of 104.7 ($C_5H_{10}O_2 = 102$). Chevreul, the original discoverer of valeric acid, which he isolated from porpoise oil and called "phocenic acid," prepared barium salts of volatile fatty acids equivalent to 9.63% of valeric acid, so that the composition of the oil is evidently very variable. From a sample of oil from *Globicephalus melas* Chevreul prepared barium salts corresponding to 20.6% of valeric acid, besides a con-

Description	Porpoise body oil					Blackfish body oil		Porpoise jaw oil					Black-fish jaw oil	Kelley's superfine (American) watch oil
Authority	Allen	Bull	Steenbuch	Schneider and Blumenfeld	Thomson and Dunlop	Bull	Moore	Moore	Moore	Moore	Steenbuch	Bull	Moore	Archbutt and Deeley
Source, etc.		American		From Phocaena communis				Unstrained	Skimmed and Strained	Skimmed and Strained		American	Skimmed and Strained	
Sp. gr. at 15°		0.9258		0.9334	0.9352	0.9266						0.9258		
Sp. gr. at 15.5°	0.926													0.930
Butyro-refractometer, 25°				62.7	54.8									
Butyro-refractometer, 40°					46.3									
Free (oleic) acid, %		nil.		0.6	0.10	0.38						2.5		
Total volatile acids, as valeric acid, %							2.71	1.64	19.91	24.30			28.17	
Unsaponifiable matter, %		3.7			0.67	2.01						16.4		10.6
Iodine value[1]		119.4		111.2 H	88.3 W	126.9	99.5	76.8	49.6	30.9		21.5	32.8	
Saponification value	216.0–218.8	195.0		224.8	256.6	203.4	197.3	143.9	253.7	272.3		269.3	290.0	
Hehner value				85.5			93.07	96.50	72.05	68.41			66.28	
Reichert value, 2.5 grm.	11–12							2.08	47.77	56.00				
Reichert-Meissl value			46.9	42.1	81.4		5.60				131.6		65.92	115.1
Mixed Fatty Acids.														
Sp. gr. at 15°				0.9121										
Solidifying-point				18.0°										
Iodine value				126.0										
Neutralisation value				207.0										

[1] H = Hübl. W = Wijs.

siderable proportion of spermaceti. Hence the oils from the Delphinidæ appear to form an intermediate group between those of the sperm whales and the whalebone whales.

The different percentages of volatile acid found is no doubt due to the difference in composition between the body oils and the jaw oils. Steenbuch found valeric acid to constitute 10% of the soluble acids of the body oil and 26% of the acids from the jaw oil. Moore obtained volatile acids equivalent to 19.91 and 24.30% of valeric acid from two samples of jaw oil, but only 2.71% from a sample of body oil.

Owing to its peculiarity of composition, porpoise oil has a high saponification value and Reichert-Meissl value. It is saponified with great facility by aqueous potash, the product being coloured reddish-brown. With the elaidin test, porpoise oil gives but little solid elaidin. The results of examination of a number of samples of these oils are given in the table on p. 231.

XI. SPERM OIL GROUP.

Sperm Oil. Arctic Sperm Oil. Bottlenose Oil.
Dolphin Oil.

SPERM OIL.

(See pp. 73 and 234.) Sperm oil proper is obtained from the head-cavities and blubber of the cachelot or sperm whale (*Physeter macrocephalus*). Several other of the toothed whales (*Odontoceti*) yield allied products, and the oil from one of these, namely, the doegling, or bottlenose whale (*Hyperoodon rostratum*) is known under the name of "Arctic sperm oil."

Sperm oil on cooling readily deposits crystalline scales of spermaceti. This is removed by filtration, but unless the operation be conducted at a very low temperature a portion of the wax is liable to remain in solution.

In the oil refineries at San Francisco the crude sperm oil is separated by refrigeration and pressing into: 1. "winter sperm oil," congealing below 38° F., the yield being about 75%; 2. "spring sperm oil," congealing at 50° to 60° F., 9%; 3. "taut-pressed oil," melting at 90° to 95° F., 5%; and 4. "crude spermaceti," melting at 110° to 115° F. 11% (United States Fish Commission Report, 1902).

Sperm oil is a thin yellow liquid, and when of good quality is nearly free from odour. Inferior specimens have an unpleasant fishy smell and taste. Its sp. gr. is very low, ranging between 0.875 and 0.884 at 15.5°.[1]

Sperm oil is one of the most valuable oils in commerce. It has been found preferable to any other fixed oil for lubricating the spindles of cotton and woollen mills and for light machinery generally, owing to its limpidity and freedom from tendency to "gum."

Some indication of the peculiar composition of sperm oil was given in 1823 by Chevreul. Chevreul's observations seem to have been wholly forgotten until Allen some years since called attention to the unique constitution of sperm oil.

Sperm oil gives on saponification products very different from those yielded by ordinary oils. When saponified with potassium hydroxide it forms potassium oleate and monohydric alcohols, the nature of which is at present unknown. By agitating the aqueous solution of the resultant soap with ether, the higher alcohols are dissolved, and may be recovered by evaporating the solvent. The fatty acids may be isolated by acidifying the soap solution and again shaking with ether. From the residual liquid glycerol can be obtained, though in much smaller proportion than from most other oils and fats. The existence of glycerol has been proved by Fendler[2] and Dunlop,[3] whose results are given in the following table:

Oil	Wax alcohols, %	Glycerol, %	Authority
Sperm	39.17	1.32	Fendler.
Cachalot "head"	41.16	2.51	Dunlop.
Cachalot "head"	42.28	1.53	Dunlop.
Cachalot "body"	44.30	1.36	Dunlop.
Arctic sperm	38.02	2.56	Dunlop.
Arctic sperm	39.22	2.26	Dunlop.

The higher alcohols, isolated in the manner described above, form a pale yellow, solid, semi-crystalline substance, the m. p. of which depends on the completeness with which the oil had been previously purified from spermaceti. They are insoluble in water, but readily soluble in alcohol and ether, and are volatile apparently without change in a vacuum, condensing as a perfectly colourless liquid, of 0.830 sp. gr. at 100°, which solidifies on cooling to a crystalline mass. The ether-residue from sperm oil is apparently a mixture of homologous alcohols which, according to Lewkowitsch[1] belong for the most part, if not wholly, to the ethylene series. Dunlop has published the following results of examination of the unsaponifiable matter (wax alcohols, etc.) from six authentic samples of sperm oil from which the spermaceti had been removed:

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[1] Dealers in sperm and similar oils commonly use a special hydrometer, devised by Casartelli, on the scale of which water is 0° and rape oil 28°. Sperm oil stands at 44° to 46° and southern whale oil at about 24° on the same scale.

[2] *Chem. Zeit.*, 1905, **29**, 555.

[3] *J. Soc. Chem. Ind.*, 1908, **27**, 64.

Description	Iodine value (Wijs)	M. p.,°	Butyro-refractometer	
			25°	40°
1a. Cachalot oil from "head-matter"	60.43	32–32.5	...	35.0
1b. Cachalot oil from "body-matter"	83.17	24.5–25.5	47.0	39.0
2a. Cachalot oil from "head-matter"	53.7	31.5–32.5	....	35.0
2b. Cachalot oil from "body-matter"	79.77	23–24	47.0	....
3. Arctic sperm oil	80.35	23.5–24	46.7	38.7
4. Arctic sperm oil	69.4	23	46.2	38.2
5. Southern sperm oil	68.5	26.5	45.7	37.7
6. Southern sperm oil	69.37	....	....	....

The following table contains some further results given by the mixed alcohols from Southern sperm (S), Arctic sperm (A), and genuine commercial oil (C) the origin of which was unknown:

	Lewkowitsch	Archbutt
Sp. gr. at $\frac{15.5^\circ}{15.5^\circ}$	....	$0.8535–0.8588^{C}$
Sp. gr. at $\frac{100^\circ}{100^\circ}$	....	0.8271^{C}
Solidifying-point, °	$23.0–23.4^{S}$ $21.7–22.0^{A}$	....
M. p., °	$25.5–27.5^{S}$ $23.5–26.5^{A}$	....
Iodine value	$64.6–65.8^{S}$ $64.8–65.2^{A}$	$65.6–69.3^{C}$ ....
Acetyl saponification value	....	184.9^{S} 186.2^{A}

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[1] *J. Soc. Chem. Ind.*, 1892, 11, 134.

The fatty acids from sperm oil appear to be mainly unsaturated acids of the oleic series, with small quantities of saturated acids and of acids more unsaturated than oleic. Fendler obtained from the mixed fatty acids of an authentic sample of sperm oil, by the lead-salt-ether method, 14.22% of saturated acids and 87.58% of unsaturated acids. Bull, by the sodium-salt-ether method, obtained from four samples of sperm and Arctic sperm oils quantities of highly unsaturated acids ranging from 3.65% (Arctic sperm) to 7.53% (Southern sperm), and absorbing from 121.2 to 159.5% of iodine.

The following results have been recorded for the mixed fatty acids of sperm and Arctic sperm oils:

	Sperm oil	Arctic sperm oil	Authority
Sp. gr. at 15°	0.8999	....	Fendler
Sp. gr. at 15.5°	0.899	....	Allen.
Solidifying-point, °	12.4	....	Fendler.
Solidifying-point (Bach), °	16.1	10.0	Archbutt and Deeley.
Solidifying-point (titer test), °	11.1–11.9	8.3–8.8	Lewkowitsch.
M. p., °	18.8	....	Fendler.
M. p., °	....	10.3–10.8	Lewkowitsch.
M. p., °	13.3	....	Williams.
M. p. (Bach), °	21.4	16.1	Archbutt and Deeley.
Iodine value	83.2–88.1	82.2–83.3	Lewkowitsch, Williams.
Mean molecular weight	281–294	....	Allen.
Mean molecular weight	305	....	Williams.
Mean molecular weight	237.7	....	Fendler.
Neutralisation value	236.2	....	Fendler.

Examination of Commercial Sperm Oil.—The peculiar physical characters and chemical constitution of sperm oil afford ample means for its detection and estimation in presence of other oils. This is important, as the high price of sperm oil renders it liable to be mixed with or replaced by other oils.

No means of distinguishing sperm and Arctic sperm oils by chemical tests is known. In commerce they are distinguished by their taste and smell, and the fatty acids of sperm oil appear to have a somewhat higher m. p. than those of Arctic sperm oil, but in other respects they are so much alike that it is convenient to consider them together.

Authentic samples of the two oils examined by Archbutt and Deeley[1] gave the following results:

Description	1 Finest southern sperm oil	2 Deodorised Arctic sperm oil
Colour	Dark golden yellow	Paler than No. 1.
Smell	Slight fishy	Fishy; more pungent than No. 1.
Sp. gr. at 15.5°	0.8809	0.8787
Viscosity (absolute) at 15.5°	0.3915	0.4148
Freezing-point	Practically solid at 0°	
Oleo-refractometer reading at 22°	−13	−13
Free (oleic) acid, %	1.2	1.6
Unsaponifiable matter, %	39.1	39.7
Maumené test; 50 grm. oil, 10 c.c. of 97% sulphuric acid	46.0°	44.8°
Saponification value	120.0	125.0
Iodine value	84.4	81.5
Mixed Fatty Acids.		
M. p. (Bach), °	21.4	16.1
Solidifying-point (Bach), °	16.1	10.0
Mixed Alcohols.		
Acetyl saponification value	184.9	186.2

A number of samples of southern and Arctic sperm oil, obtained from reliable sources, have been examined by Dunlop,[2] whose results are given in the following table:

		Cold test, °	Sp. gr. at 15.5°	Butyro-refractometer, 25°	Free (oleic) acid, %	Wax alcohols, etc., %	Iodine value (Wijs)	Saponification value
1a	Cachalot oil from "head matter"	9.5	0.8779	49.7	4.60	42.28	76.30	140.2
1b	Cachalot oil from "body matter"	8.5	0.8772	54.8	1.42	42.14	92.85	124.8
2a	Cachalot oil from "head matter"	7.0	0.880	50.0	1.39	41.16	70.35	144.4
2b	Cachalot oil from "body matter"	7.0	0.8757	54.6	1.07	44.30	87.90	122.0
3	Arctic sperm oil	......	0.8806	55.2	0.73	38.02	88.75	129.0
4	Arctic sperm oil	......	0.8786	55.3	1.43	39.22	82.80	124.8
5	Southern sperm oil	......	0.8791	54.6	1.16	41.16	84.35	129.7
6	Southern sperm oil	......	0.8798	......	2.53	39.20	84.37	129.0

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[1] Lubrication and Lubricants, 1907, p. 325.

[2] *J. Soc. Chem. Ind.*, 1908, **27**, 64.

The oils numbered 1 and 2, from 2 animals, represent the oil after removal of the spermaceti from the "head" and "body" matter, respectively; these oils are not usually kept separate in practice, but are mixed together, and hence the differences in the iodine and saponification values, though noteworthy, are not of practical importance.

The *sp. gr.* of genuine commercial sperm oil ranges from 0.878 to 0.884 at 15.5°. In the absence of mineral oil, Dunlop considers that a figure within 0.875 and 0.882 will generally indicate a pure oil. Adulteration with any other fixed oil would raise the gravity, but this could be corrected by the addition of light mineral oil.

The *saponification value* of genuine sperm oil appears to range from about 120 to 137. It would be raised by the addition of a fixed oil and lowered by that of mineral oil, but a mixture of the two might be added having the same saponification value as sperm oil.

The nature and estimation of the saponification-products afford the most satisfactory means of detecting adulterations of sperm oil, which, when genuine, yields from 60 to 63% of insoluble fatty acids, and 37 to 42% of ether-residue consisting of higher alcohols. No other animal or vegetable oil, except shark-liver oil and oils from allied *Cetacea* (*e. g.*, bottlenose oil), is known to yield more than 2% to ether, and, with few exceptions (*e. g.*, porpoise oil and some varieties of whale oil), all other fixed oils yield fully 95% of insoluble fatty acids, and from 10 to 12% of glycerol. Hence, in a case of adulteration of sperm oil with any other fatty oil, estimation of the ether-residue will detect the admixture and approximately estimate the proportion. Some specimens of shark-liver oil yield a considerable proportion of ether-residue, and hence if shark oil be present the ether process will be rendered inaccurate. Genuine shark-liver oil has a comparatively high sp. gr., 0.911 to 0.929, and has a very high halogen-absorption, besides giving a well-marked violet colouration and great increase of temperature with strong sulphuric acid.

The foregoing process, if used without discretion, would fail in the case of a mixture of mineral oil and a fatty oil in certain proportions, but a careful consideration of the results and further examination of the products will allow of such a mixture being readily distinguished from sperm oil. Thus from an inspection of the figures in the following table it appears that while the saponification-products yielded by sperm oil would be approximately simulated by those given by a judicious mixture of mineral oil with rape oil, in the latter case the sum of the fatty acids and ether-residue would be several units less than 100, and there would be a larger proportion of glycerol produced. Besides, the ether-residue would probably be insoluble in cold rectified spirit (see below), and to obtain a mixture of the same sp. gr. as sperm oil, so very light a mineral oil would require to be used that it would necessarily be liquid, even at 0°, and would have so low a flashing-point that it could without difficulty be detected in, and even distilled out of, the original oil or the ether-residue. Sperm oil does not flash below 400° F.

	Products of the saponification of 100 parts of oil			
	Fatty acids	Glycerol	Ether-residue	
			Percentage	Characters
Sperm oil	60 to 64	1.3 to 2.6	37 to 42	Solid; soluble in spirit.
Ordinary fixed oils	95 to 96	10 to 11	0.5 to 1.5	
Mineral oil	none	none	100	Liquid; insoluble in spirit.
Rape oil, 60, Mineral oil, 40,	57.6	6	40	Liquid; insoluble in spirit.

Although mineral oils are practically insoluble in rectified alcohol, Nash[1] has shown that a solution of sperm-oil alcohols in absolute alcohol, and even in alcohol of 0.8345 sp. gr., unless much diluted, dissolves mineral oil freely. Absolute alcohol must, therefore, not be used in testing the unsaponifiable matter for mineral oil; but if the unsaponifiable matter from 5 grm. of a sperm-oil sample be normal in amount and completely soluble in 50 c.c. (not less) of cold alcohol of 0.834 sp. gr., the sample is most probably genuine. Dunlop states, however, that even under these conditions a considerable amount of mineral oil may be dissolved and lost sight of. The following tests for mineral oil are, however, available:

Holde's Test.—6 to 8 drops of the oil are boiled in a test-tube for 2 minutes with 5 c.c. of N/2 alcoholic potassium hydroxide, and to the soap solution thus prepared distilled water is added very gradually, well mixing after each addition, until from 0.5 to 15 c.c. have been added altogether. If mineral oil be absent, the solution remains clear, even when mixed with the maximum quantity of water, but the presence of even 1% of mineral oil is said to cause the formation of a turbidity.

[1] *Analyst*, 1904, 29, 3.

Careful observation is needed, since the characteristic feeble turbidity caused by a very small proportion of mineral oil, which appears after the addition of the first few drops of water, disappears again on adding more and may easily be overlooked. Rosin oil is said not to be detectable in less quantity than 12%. The higher alcohols in sperm oil do not interfere, since they remain dissolved in the soap solution for some time (Lobry de Bruyn). Dunlop found this test capable of detecting as little as 3.5% of mineral oil.

Flashing-point.—Of 93 samples of sperm oil tested by Veitch Wilson the flashing-points (closed test) of only 3 samples were below 410° F., viz.: 1 sample 400° and 2, 390°. The others ranged from 410° to 485° F., and the averages were 457.5° F. for southern sperm oil and 446.2° F. for Arctic sperm oil. Several samples of genuine sperm oil tested by Dunlop in Gray's apparatus flashed at from 410° to 422° F. A mixture of sperm oil flashing at 416° F. with 5% of "0.865" mineral oil flashed at 361° F., and with 5% of "0.896" mineral oil at 392° F. A flashing-point below 410° F. would be suspicious, and below 400° F. would probably indicate adulteration.

Dunlop points out that the *refractive power of the unsaponifiable matter* may be useful for the detection of mineral oil. The highest butyro-refractometer reading he has obtained for the mixed alcohols of genuine sperm oil is 47 scale divisions at 25°. The addition of 10% of "0.865" mineral oil would raise this by about 6 units.

For the detection of fish oils and blubber oils in sperm oil, the estimation of the *yield of insoluble brominated esters* may prove useful. Walker and Warburton obtained from 2 samples of sperm oil only 2.5 and 3.7%, respectively, of brominated esters insoluble in ether, while all other fish and blubber oils which have been tested have given a much larger yield. Dunlop obtained the following results by Procter and Bennett's method:

	"Bromide value," = yield % of brominated esters insoluble in a mixture of CCl_4 and alcohol
1. Cachalot oil from "head matter"	1.13
2. Cachalot oil from "body matter"	2.00
3. Cachalot oil from "body matter"	2.30
4. Arctic sperm oil	3.04
5. No. 2 with 10% of whale oil	3.68

As whale oils were found by Procter and Bennett to yield from 27 to 37% of brominated esters, a greater difference between the yield from oil No. 2 and mixture No. 5 might have been expected. But further experiments are needed. Procter and Bennett themselves obtained 6.3% of brominated esters from the sperm oil which they tested.

In examining sperm oil the *iodine value* is not so useful or so necessary a test as in the case of other oils. The recorded values have a fairly wide range, Dunlop's figures ranging from 70.3 to 92.8 (Wijs), but as these extreme values were obtained from head-matter oil and body-matter oil, respectively, and not from the mixed oil, they must be regarded as abnormal. A range from 80 to 90 would include most genuine commercial sperm oils, though Bull records a value as low as 67.1 (probably obtained by the Hübl method) for an Arctic sperm oil containing 42.61% of unsaponifiable matter and having a saponification value of 122.3. Dunlop has pointed out that there is a relationship between the iodine value of the wax alcohols and that of the oil. This will be seen by comparing the iodine numbers given in the table on p. 234 with those in the table on p. 236 from the same oils. The difference in the amount of iodine absorbed by different oils would, therefore, appear to be due partly to the variable composition of the alcohols.

Sperm oil has a much lower viscosity than most fixed oils, and this physical property in absolute measure is given on p. 236. The efflux time of 50 c.c. of sperm oil from Redwood's viscometer has been stated as follows: at 60° F., 177 to 201 seconds; at 70° F., 137 to 164 seconds. Southern sperm oil seems to be rather lower in viscosity than Arctic sperm, but more samples need testing.

The colour indication with sulphuric acid (page 41) is often a useful test for the purity of sperm oil. The genuine oil gives a brown colouration, becoming somewhat darker with a tinge of violet on stirring. Shark-liver oil gives a well-marked violet colour when tested in the same manner, the tint changing to red or reddish-brown on stirring.

ARCTIC SPERM OIL. DOEGLING OIL. BOTTLENOSE OIL.

(See also page 73.) Several species of toothed cetaceans yield an oil analogous to that obtained from the cachelot or sperm whale. The chief of these in economic importance is the product from the doegling or bottlenose whale (*Hyperoodon rostratum*),[1] which is known in commerce as "Arctic sperm oil."

Bottlenose oil deposits more or less spermaceti when cooled, but the yield is not nearly so large as that obtained from the head matter and oil of the sperm whale, though of good quality and high m. p. Bottlenose oil often has a more or less unpleasant odour, but this peculiarity, together with the small proportion of free acid present in the crude oil, can be removed to a great extent by agitation with a solution of sodium carbonate or by analogous treatment. The refined oil is straw-yellow.

The chemical constitution of doegling oil was first pointed out by Scharling (*Jour. Prakt. Chem.*, 1848), who found it to consist essentially of the ester of a higher monatomic alcohol, dodecyl doeglate, $C_{12}H_{25}.C_{19}H_{39}O_2$ and hence to yield on saponification dodecyl alcohol and doeglic acid. Further investigation on this point is desirable. Bull thinks that Scharling's doeglic acid ($C_{19}H_{36}O_2$) must have been a mixture of gadolinic acid ($C_{20}H_{38}O_2$) (see under "Cod-liver Oil") and oleic acid ($C_{18}H_{34}O_2$).

The wax alcohols, etc., obtained from bottlenose oil by agitating the aqueous solution of the saponified oil with ether and separating and evaporating the ethereal solution, have similar characters to the product obtained in a similar manner from sperm oil (see under "Sperm Oil").

The mixed fatty acids prepared by Allen from several specimens of bottlenose oil were found to have a sp. gr. of 0.896, their combining weights ranging from 275 to 294.

Bottlenose oil presents the closest resemblance to sperm oil. In its sp. gr. (0.876–0.881), viscosity, solubility in acetic acid, saponification-equivalent, and behaviour with strong sulphuric acid and the elaïdin-test, it presents no tangible difference from sperm oil. On saponification it yields from 61 to 65% of fatty acids, and from 37 to 41% of ether-residue, in this respect simulating true sperm oil in the closest manner. The only differences observed by Allen in the course of a series of very careful comparative examinations of sperm and doegling oils have been the slight tendency of the latter to gum or thicken on exposure, and the somewhat higher m. p. of the fatty acids from sperm oil. It has, therefore, been convenient to treat them together in the preceding pages under the "Examination of Commercial Sperm Oil."

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[1] There has been much confusion respecting the bottlenose, at least eight different whales and dolphins having been designated by that name.

DOLPHIN OIL.

The oil from the blubber of the blackfish, *Globicephalus melas*, is citron-yellow in colour, deposits spermaceti when cooled, and contains a large proportion of the glyceride of valeric acid. It presents many points of resemblance with porpoise oil (see under "Porpoise Oil").

XII. BEESWAX GROUP. SOLID WAXES.

Beeswax.	**Chinese Insect Wax.**
Carnauba Wax.	**Spermaceti.**

Wool Fat. Wool Wax.

BEESWAX.[1]

(See also table on page 73.) Beeswax is the material of which the honeycomb of bees is composed. To obtain the wax the honey is drained off, the comb expressed, melted in water, the impurities allowed to subside, and the wax allowed to cool or run into suitable moulds. About 1 pound of wax is obtained from 20 pounds of honey. In the process, as described by Hirschel,[2] the bulk of the wax is first separated by treatment with hot water and straining from dead bees, etc., and the residue pressed in layers with straw in a filter-press. The pressed residue is again boiled with water and pressed, after which there still remains 10 to 15% of wax in the press-cake. This is extracted with petroleum spirit and known as "*extraction wax*," the former being "*pressed wax*." 3 samples of genuine "extraction wax" examined by Hirschel, previous to bleaching and refining, were dark brown, soft, greasy substances, of unpleasant odour. They had higher acid values than normal beeswax (23.3 to 27.1) and lower "ratio numbers" (2.46 to 2.95), also much higher iodine values (31.2 to 39.6); the m. p. (61.3° to 62.5°) and sp. gr. at 15° (0.953 to 0.957), though lower than, did not differ greatly from those of ordinary beeswax. All three samples gave faint indications for rosin, and in Weinwurm's test (page 257) behaved as if containing about 5% of paraffin wax.

Yellow Wax.—Normal beeswax is a tough, compact, solid substance, of a yellowish or brownish colour, with a slight lustre and a finely granular fracture. Its taste is faint and slightly balsamic, and the odour is honey-like and characteristic. It does not feel greasy to the touch.

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[1] Bibliographies relating to beeswax and to waxes used for adulterating it are given in *J. Soc. Chem. Ind.*, 1892, **11**, 756, 757.

[2] *Chem. Zeit.*, 1904, **28**, 212.

Beeswax can be volatilised almost without change in a vacuum. When distilled under the ordinary pressure, it yields a variety of products, among which acrolein does not appear to occur. It is insoluble in water, but dissolves readily in fixed oils, carbon disulphide, and in about 10 parts of boiling ether or turpentine. According to Hager, ether dissolves only about half the wax at the ordinary temperature, and benzene and petroleum spirit about 27%.

Buchner,[1] with cold ether, separated beeswax into two portions, giving the following results as compared with the original wax:

	Acid value	Ester value
Original wax	19.5	76.7
30% dissolved by ether	40.0	43.8
70% undissolved by ether	11.6	87.5

Yellow beeswax is completely soluble in chloroform (Dieterich). It is nearly insoluble in cold alcohol, but dissolves in about 300 parts of the boiling liquid, leaving only a small yellowish-brown residue. On cooling, the solution deposits a whitish crystalline substance, while the filtrate is yellowish, and is not rendered turbid by addition of water. The portion soluble in cold alcohol consists of aromatic and colouring matters, together with a small quantity of fatty matter to which the name of cerolein has been given. The portion of beeswax dissolved by a moderate quantity of hot alcohol consists chiefly of cerotic acid and its homologues, while the undissolved part is myricin.

Schwalb[2] separated from beeswax about 6% of hydrocarbons of the paraffin series, among which he identified heptacosane, $C_{27}H_{56}$, melting at 60.5°, and hentricontane, $C_{31}H_{64}$, melting at 67°. Much larger quantities of hydrocarbons have since been found by Buisine and others (see page 260).

T. Marie[3] has shown that the free acids of beeswax consist of cerotic acid, mixed with from 30 to 40% of homologous acids, including melissic acid.

Cerotic acid, $C_{26}H_{52}O_2$ (Lewkowitsch), dissolves in hot ethyl alcohol, but is almost wholly deposited on cooling; when quite pure, it forms stellate, microscopic needles, melting at 77.9°. It is easily soluble in warm methylic alcohol and ether. *Melissic acid*, $C_{30}H_{60}O_2$, resembles cerotic acid in appearance, but crystallises more readily and melts at 90.6°. It is readily soluble in hot ethyl alcohol, chloroform, petroleum spirit, and carbon disulphide, but almost insoluble in warm methyl alcohol and ether. For the properties of these acids and their derivatives and the method of separating them in a pure state from beeswax, the papers by Marie should be consulted. The proportion of crude cerotic acid existing in beeswax in the free state usually ranges from 12 to 16%.

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[1] *Chem. Zeit.*, 1907, **31**, 570.

[2] *Chem. Centr.*, (3), **16**, 354; *Annalen*, 1886, **235**, 149.

[3] *Compt. rend.*, 1894, **119**, 428; *J. Pharm.*, 1896, (6), **3**, 107; *Bull. Soc. Chim.*, 1896, (3), **15**, 503, etc.

Myricin is the chief constituent of beeswax insoluble in alcohol. It is a solid, wax-like body, melting at 64°. On saponification, it yields a palmitate, myricyl alcohol, and a small quantity of soap from an acid of the oleic series. Hence myricin has essentially the constitution of myricyl palmitate.

Myricyl alcohol, $C_{30}H_{61}.OH$, may be prepared by heating myricin or beeswax itself in a closed vessel for an hour or 2 with excess of alcoholic potassium hydroxide, nearly neutralising the excess with acetic acid (using phenolphthaleïn as an indicator), and precipitating the turbid liquid with excess of lead acetate. The precipitate, consisting of a mixture of lead soaps and myricyl alcohol, is washed, dried, and exhausted with hot ether or petroleum spirt in a Szombathy tube. On evaporating the solvent, the wax-alcohol is obtained in white glittering crystals, which may be purified by washing with cold alcohol and recrystallisation from ether. It may also be prepared in a similar manner from carnaüba wax.

Myricyl alcohol is a crystalline silky substance, melts at 85° to 86° to a colourless liquid, and solidifies to a fibrous mass at about 1° lower. It is insoluble in water, scarcely soluble in cold alcohol, ether, or benzene, and but little in cold chloroform. It dissolves readily in boiling alcohol, ether, chloroform, benzene, and petroleum spirit. When fused with potassium hydroxide, or heated to 220° with potash-lime as long as hydrogen is evolved, it is converted into potassium melissate, $KC_{30}H_{59}O_2$, which, on solution in water and treatment with an acid, gives melissic acid.

White or Bleached Wax.—By exposure to moisture, air, and light, beeswax becomes decolourised. It is usually exposed to sunlight in thin cakes, but the bleaching is a slow process. In order to expose as large a surface as possible, Ramboe[1] has proposed to break the wax up into minute globules by emulsifying it with hot water and pouring the emulsion into cold water to which a little oil of turpentine has been added. Wax thus subdivided, if previously mixed with bleached wax, can be bleached by sunlight in 3 or 4 days. The addition of bleached wax to the yellow wax is found to greatly reduce the time required for bleaching.

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[1] *Chem. Zeit.*, 1896, 20, 1004.

Beeswax may also be bleached by cautious treatment with chromic or nitric acid; but chlorine cannot be advantageously employed owing to the formation of chlorinated substitution-products which give rise to hydrochloric acid when the wax is burnt. It may also be bleached by boiling it with a dilute solution of potassium dichromate and sulphuric acid. The wax thus treated has a greenish colour from the presence of chromium compounds, which it holds very persistently, but which may be removed by boiling the product one or more times with a solution of oxalic acid. Permanganate bleaching is also employed. It is not every kind of wax which can be effectually bleached. The presence of a small proportion of fatty matter appears to facilitate the process.

The effect of bleaching on the constants of beeswax has been studied by Buisine,[1] Berg,[2] and others. The *acid value* is raised, least by natural, most by chromic acid bleaching, to a sufficient extent to lower the ratio number and suggest adulteration with stearic acid. Thus, Buchner has recorded the following numbers for chemically bleached wax: acid value, 23.1 to 26.2; saponification value, 95.0 to 98.45; ratio number, 2.70 to 3.20. The *saponification value* of bleached wax is always a few units higher than that of the yellow wax. Berg found the *iodine value* lowered by the natural and permanganate methods of bleaching, but, curiously, raised by chromic acid bleaching, except in the case of Italian waxes, which had their iodine values lowered in all cases. Dieterich found the iodine value of bleached wax 4.2 to 4.4. *Buchner's number* is slightly lowered by natural and permanganate bleaching; chromic acid sometimes raises it considerably, sometimes does not alter it, or even lowers it in the case of Italian waxes. Natural and permanganate bleaching either do not affect or slightly raise the *refractive power* of the wax; treatment with chromic acid or any method of bleaching Italian wax lowers the refractive power. Chromic acid frequently raises the m. p.; other processes lower it a trifle. A Morocco wax bleached by chromic acid had its m. p. raised from 64.5° to 67.5°. Medicus and Wellenstein[1] found the m. p. of a wax raised from 62.5° to 63.5° by chromic acid bleaching, that of the mixed free fatty acids being raised from 68° to 69°, and their acid value from 51.47 to 58.83. An ultimate analysis gave $C_{28}H_{56}O_2$ or $C_{29}H_{58}O_2$ for the yellow wax and $C_{24}H_{48}O_2$ or $C_{25}H_{50}O_2$ for the bleached wax. Théy attribute the increased acidity to the splitting up of the acids with formation of acids of lower molecular weight. White wax is not completely soluble in chloroform (Dieterich).

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[1] *Bull. Soc. Chim.*, 1890, [3], **4**, 465, in which detailed results are given of yellow waxes before and after bleaching by several methods; also *Compt. rend.*, 1891, **112**, 738.

[2] *Chem. Zeit.*, 1902, **26**, 605.

Analysis of Genuine Beeswax.—The proportion of crude *cerotic acid* in beeswax can be ascertained by titration with standard acid and phenolphthaleïn in the usual way, but, owing to the very high combining weight of the acid, the operation must be conducted with extreme care. Hehner[2] recommends that alcoholic potassium hydroxide should be used, and that it should be prepared from pure material and from spirit which has been redistilled from potassium hydroxide. It should be about N/3—that is, 1 c.c. should correspond to 0.3 to 0.4 c.c. of N/1 acid. The alkali should be standardised several times with the acid, and the results should not differ by more than 0.05 c.c. of standard alkali for each 10 c.c. of acid used. 5 grm. of the wax should be heated in a flask with 50 c.c. of methylated spirit which has been redistilled from sodium hydroxide. When the wax is perfectly melted, an alcoholic solution of phenolphthaleïn is added in not too small an amount. The indicator must not be acid, as is frequently the case, but must previously have been rendered pink by addition of alkali in faint excess. The standard solution of alcoholic alkali is then added drop by drop, the liquid being kept well agitated until the pink colour becomes permanent, when the volume employed is observed. The combining weight of cerotic acid being 410 (based on Brodie's formula, $C_{27}H_{54}O_2$. As a matter of fact, the mean molecular weight of the free acid in beeswax has been found by Hehner to be 407); a volume of standard alkali corresponding to 1 c.c. of normal acid represents 0.410 grm. of cerotic acid. The percentage of cerotic acid may be found by multiplying the percentage of potassium hydroxide required for neutralisation by 7.31. As the volume of standard alkali required by 5 grm. of wax amounts to only a few cubic centimetres, a very finely graduated burette should be employed.

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[1] *Zeit. Nahr. Genussm.*, 1902, **5**, 1092.
[2] *Analyst*, 1883, **8**, 16.

Hehner found by this process, in sixteen samples of English unbleached wax, proportions of free acid, calculated as cerotic acid, ranging from 12.15 to 15.71%, the average being 14.4. 17 samples of foreign wax gave very similar results, but showed a somewhat wider variation, the extreme numbers obtained being 12.17% from a dark-brown Mauritian wax, which showed signs of having been burnt in the process of manufacture, and 16.55% from a dark-brown wax from Gambia. In wax bleached by air and light the proportion of free acid is practically unchanged, but in wax bleached by chromic acid mixture it may be increased to 17 or 18%. Thus, in 24 samples of commercial bleached wax Hehner found from 15.5 to 17.6% of free acid calculated as $C_{27}H_{54}O_2$, the average being 16.6% or almost exactly one-sixth of the wax. Hehner's results have been confirmed by Hübl,[1] who found in 20 samples of yellow wax proportions of free acid ranging from 13.9 to 15.3, the average being 14.6%.

It is evident that the foregoing rapid and simple volumetric process fails to prove the actual nature of the free acid, but by operating on a somewhat larger quantity of beeswax the same method serves as the first step toward the actual isolation of cerotic acid, the quantity obtained being sufficient for the estimation of the fusing-point and other data. The unsaponified portion consists principally of *myricin* and hydrocarbons, which can be separated and weighed as such, or its nature and composition may be deduced from the results of its saponification in the following manner:

The experiment by which the proportion of crude cerotic acid in beeswax was ascertained by titration with alcoholic alkali and phenolphthaleïn may be extended in such a way as to obtain an estimation of the *myricin*. For this purpose a further exactly known volume of standard alcoholic potash should be run into the flask, the quantity used being equivalent to about 25 c.c. of N/1 acid. A reflux condenser is then attached to the flask, and the liquid briskly boiled for 1 hour, when the solution should be clear, or nearly so. The flask should be agitated at intervals to remove any particles of wax which may have adhered to the sides of the flask above the liquid. The condenser is then detached and the solution titrated back from a very delicate burette with N/2 acid. The alkalinity which has disappeared, expressed in terms of N/1 acid, represents the myricin which has been saponified. 1 c.c. of normal acid, or 0.0561 grm. of potassium hydroxide neutralised, corresponds to 0.676 grm. of myricin. Hübl found 20 samples of yellow wax to require from 7.3 to 7.6% of potassium hydroxide for the saponification of the myricin, which figures correspond to proportions of that substance varying from 88 to 91.6%. These results fully confirm those of Hehner, who found in sixteen samples of yellow English wax proportions of saponifiable substance expressed as myricin ranging from 85.95 to 89.05, the average being 88.1, and in 24 samples of commercial bleached wax proportions ranging from 85.2 to 89.9%, the average being 87.7%.

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[1] *Dingl. Polyt. J.*, 1883, **249**, 338.

When estimated volumetrically by the above method, the free acid expressed as cerotic acid and the esters expressed as myricin together usually amount to somewhat more than 100%, the average being, according to Hehner, 102.5. It is evident, therefore, that wax requires more alkali for saponification than would be required for a mixture of pure cerotic acid and myricin.

The results above recorded prove that genuine beeswax is of approximately constant composition. Hehner's experiments show that the proportion the cerotic acid bears to the myricin in English beeswax (unbleached) averages 1 : 6.12, while Hübl finds ratios varying from 1 : 5.94 to 1 : 6.24; in English bleached wax Hehner found an average ratio of 1: 5.3.

Adulterations of Beeswax.—Commercial beeswax is liable to contain a number of adulterants, among which the following are recorded: Water; mineral matters, as kaolin, gypsum. barium sulphate, and yellow ochre; sulphur; starch and flour; resinous substances, as colophony, galipot, and burgundy pitch; fatty substances, as stearic acid, stearin, Japan wax, and tallow; paraffin and ozokerite; and vegetable waxes, as carnaüba wax. Spermaceti is also said to have been used.

Water has been met with in beeswax to the extent of 6%, being purposely introduced. It may be detected and estimated as described under "Lard."

Mineral matters may be detected and estimated by igniting the wax. They will also remain insoluble on dissolving the sample in turpentine, chloroform, or benzene. As much as 17% of *yellow ochre* has been found in unbleached beeswax.

Starch and *flour* will be left undissolved on treating the wax with warm turpentine. The liquid may be filtered, the residue washed with a little ether, and examined under the microscope with solution of iodine. 60% of starch has been met with. Small quantities of starch or flour may exist in genuine wax that has been rolled or pressed, the rollers or press being dusted over with flour to prevent the wax from sticking.

Sulphur has been found as an adulterant of unbleached wax. It may be detected by boiling the sample with a weak solution of soda, and adding lead acetate to the cooled liquid, when a black or brown precipitate will be produced if sulphur be present.

Beeswax containing any of the above-named impurities or admixtures should be melted over water, and the molten wax filtered through paper and dried in the water-oven before proceeding with the following tests.

As a useful preliminary test, the sample may be dissolved in *chloroform*, in which genuine yellow wax is completely soluble. Incomplete solubility would indicate the presence of paraffin, ceresin, carnaüba wax or wool wax (Dieterich). White wax, however, even when genuine, is not completely soluble in chloroform.

J. Werder (*Chem. Zeit.*, 1898, **22**, 38, 59) finds that the Zeiss *butyro-refractometer* may advantageously be employed in the examination of different kinds of wax, especially when the amount of material at disposal is very limited, and that the indications obtained with it are quite as valuable as in the case of oils and fats. Owing to the high m. p. of the wax, it is necessary to work at a higher temperature than usual, preferably 66° to 72°, and then to reduce the results to the normal temperature, 40°. As shown in the annexed table, the figures given by genuine beeswax vary from 42.6° to 45.4°, the great majority of specimens falling between 44° and 45°; and it seems to make little or no difference to the refractive power whether they are tested before or after bleaching. Samples 19 to 24 had previously been examined chemically, and had been rejected on the ground of their abnormal acid and ester values, which were as follows:

Number of sample	Acid value	Ester value
19	18.48	66.64
20	127.1	13.4
21	59.08	3.36
22	104.7	14.3
23	41.0	57.0
24	106.9	48.1

No. 24 is a product called "Glanzwachs," obtained by adding some of the mixture of stearic and palmitic acids as used in the manufacture of stearin candles (No. 28) to a genuine wax, this being a form of adulteration commonly employed in Switzerland.

Refractive Power of Different Kinds of Wax.

Sample	Temperature of observation	Refraction at 40°
1. Bleached, from Egypt	66.0	44.1
2. Bleached, from Turkey	67.0	44.8
3. Bleached, from Moldavia	66.5	44.2
4. Yellow, from Egypt	66.0	42.8
5. Yellow, from Monte Christo	71.0	44.8
6. Yellow, from France	67.5	44.1
7. Yellow, from Savoy	67.0	42.6
8. Yellow, from California	69.5	45.2
9. Yellow, from North Africa	71.0	45.0
10. Yellow, from Massowah	71.5	44.3
11. Yellow, from Italy — different samples	70.0	44.9
12. Yellow, from Italy	70.0	44.0
13. Yellow, from Italy	68.5	44.6
14. Yellow, from Mexico — different samples	69.5	44.2
15. Yellow, from Mexico	67.0	45.3
16. Yellow, from Syria	69.5	44.2
17. Yellow, from Casablanca	68.0	45.4
18. Yellow, from Smyrna	70.0	44.7
19. Bleached, in chips (professedly genuine)	70.5	41.3
20. White church candles (professedly genuine)	67.5	32.0
21. White church candles (professedly genuine)	68.0	32.5
22. White church candles (professedly genuine)	68.5	32.6
23. Yellow wax, source unknown	66.0	38.3
24. Wax adulterated with No. 28	65.5	38.8
25. Paraffin	65.0	22.5
26. Ceresin	77.0	41.0
27. Tallow	71.5	48.5
28. Stearin candle material	70.0	30.0
29. Carnaüba wax	91.0	66.0
30. Japan wax	71.0	47.0

The sp. gr. of beeswax is a useful indication of the presence of foreign admixtures. Great discrepancies occur in the recorded sp. gr. of possible adulterants of beeswax, as determined by various observers, the differences being probably due to the faulty methods of observation. The subject has been investigated by W. Chattaway in Allen's laboratory, with the following results:

1. Hager's method is objectionable, owing to the anomalous contraction caused by sudden cooling of the fused substance.

2. If sudden cooling be avoided, the estimation may be made by immersing the fragment in dilute alcohol or ammonium hydroxide, adjusting the sp. gr. of the liquid until identical with that of the wax, and then ascertaining its sp. gr. by one of the usual methods. To prepare the fragments, a good plan is to melt the wax in a clock-glass or flat-bottomed capsule placed over a beaker of boiling water, and then remove the source of heat and allow the water in the beaker to cool spontaneously. Small blocks can then be cut from the solidified wax with a knife, or cylinders removed with a corkborer. Another good plan is to suck up the molten wax into a piece of quill-tubing, the upper end of which is then closed by the finger, while the lower is immersed in cold water. This causes the wax to set at the orifice of the tube, and so closes it. The tube is then supported in a vertical position, and the contents allowed to solidify spontaneously. Owing to the mode of cooling, the wax forms a smooth cylindrical stick, readily removable from the tube; the central portion is always free from cavities and air-bubbles. The cubes or cylinders are then painted over with a wet brush to prevent the adherence of air-bubbles, and then cautiously lowered (not dropped) into the spirit by means of a pair of forceps or a glass rod bent into the form of a hoe.

3. In the case of a crystalline substance, such as spermaceti or Chinese wax, the estimation of the sp. gr. of the solid substance is very unsatisfactory, but the difficulty is wholly avoided if the observation be made on the molten wax at the temperature of boiling water.

The *melting- and solidifying-point* of a sample of wax will often afford valuable information; but unfortunately the figures recorded as the m. p. of various waxes exhibit great discrepancies, owing to the different methods employed.

The following table shows a number of results obtained in Allen's laboratory by the examination of specimens of waxes and analogous bodies. The sp. gr. were estimated by the methods just indicated, the m. p. by the first method on page 52, and the solidifying-points by Dalican's method, page 55:

Substance	Sp. gr.; water at 15.5° = 1.		Temperature of change of physical state; °	
	At 15–16°	At 98–99°	M. p.,°	Solidifying-point,°
Beeswax, yellow	0.963	0.822	63.0	60.5, no rise
Beeswax, chemically bleached	0.964	0.827	63.5	62.0, no rise
Beeswax, air-bleached	0.961	0.818	63.0	61.5, no rise
Spermaceti, bottlenose	0.942	0.808	49.0	48.0, no rise
Carnaüba wax	....	0.842	85.0	81.0, no rise
Chinese insect wax	....	0.810	81.5	80.5, no rise
Japan wax	0.984–0.993	0.875–0.877	51–53	41.0, rising to 48
Myrtle wax	....	0.875	40.5	39.5, no rise
Tallow, pressed	....	0.861	44.5	32.5, rising to 34
Suet, beef	0.944	0.860	49.0	32.5, rising to 34.5
Stearic acid	....	0.830	56.5	54.5, no rise
Colophony	1.074	....	....	....
Paraffin wax	0.909	0.753	54.5	54.0, no rise
Ozokerite, refined	....	0.753	61.5	60.0, no rise

The following table gives the sp. gr. and m. p. of waxes and some other substances, as estimated by other observers:

Substance	Sp. gr. at 15°–15.5°	M. p.,°	Solidifying-point,°
Beeswax, yellow	0.959–0.970	62.5–64.5	60.5–63.5
Beeswax, bleached	0.966–0.968[1]	62–70	61.6
Spermaceti	0.905–0.960	41–46	41–47
Carnaüba wax	0.995–1.000	83–86	....
Japan wax	0.976–0.993	50.4–53.4	48.5–51
Tallow	0.937–0.953	38–49	27–36
Stearic acid	0.964–0.986	58–65	....
Colophony	1.070–1.090	....	....
Paraffin wax Ceresin	0.868–0.915	48–72	....

The most valuable method for the examination of beeswax is based upon the researches of Hehner and Hübl, and consists in a careful estimation of the *acid value* and *saponification value* of the sample. Hehner's method of operating has already been described on p. 246; Hübl's was substantially the same. Numerous modifications have since been proposed.

Thus, Henriques[2] has proposed a method of cold-saponification, in which the wax (3 to 4 gr.) is dissolved in 25 c.c. of warm petroleum spirit (boiling at 100°–150°), titrated with N/2 alcoholic sodium hydroxide made with 96% alcohol for estimating the acid value, then mixed with N/1 alcoholic sodium hydroxide and allowed to stand for 24 hours in the cold, the saponification value being estimated by titrating the excess of alkali. There appears to be no advantage in this process, and it is slower than the ordinary method. The acid values estimated by it are lower than those estimated by Hehner's method (*Dieterich*, *Buchner*). Cohn[1] finds 3 hours' boiling with alcoholic potassium hydroxide under a reflux condenser necessary to ensure complete saponification, but others have shown 1 hour to be sufficient if strong enough alcohol (96 to 98%) be used. Buchner[2] has proposed to use a Szombathy extractor as reflux condenser, the concentration of the alkali resulting from its use helping the saponification. Eichorn[3] has suggested using amyl alcohol instead of ordinary alcohol, in order to carry out the neutralisation and saponification at a higher temperature. Berg[4] states that different waxes require different times for saponification; German seldom less than 2 hours, usually 3 to 3 1/2 hours; Morocco, about 5 hours; East African, up to 6 hours; Chinese and Tonking, up to 8 hours. He thinks every wax contains lactonic anhydrides which are difficult to saponify, differing from Buchner, who believes these substances are of only rare occurrences. In the reviser's experience, the following method of operating usually gives good results:

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[1] 24 samples examined by O. Hehner, the m. p. of which ranged from 63.4° to 64.4°.
[2] *Zeit. Angew. Chem.*, 1895, 721; 1896, 221.

8 grm. of the wax are warmed with 70 c.c. of neutralised rectified alcohol until melted, then mixed with neutralised phenolphthaleïn solution and carefully titrated with N/2 alcoholic potassium hydroxide. This gives the acid value. For ascertaining the saponification value, 5 grm. of wax are boiled under a reflux condenser for at least 1 1/4 hours with 25 c.c. of N/2 alcoholic potassium hydroxide, made with alcohol of 95 to 96% strength, and then titrated with N/2 hydrochloric acid and phenolphthaleïn in the usual way.

The difference between the acid and saponification values was termed by Hübl the "*ester value*," and he found the *ratio*, $\frac{\textit{ester value}}{\textit{acid value}}$, in genuine beeswax ranged from 3.6 to 3.8. Adulteration with unsaponifiable matters (paraffin, ceresin) lowers the saponification value without disturbing this ratio; acid substances (stearic acid, resin), raise the acid value and lower the ratio, foreign waxes or fats raise the ratio as is indicated in the following table:

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[1] *Zeit. öffentl. Chem.*, 1904, **10**, 404.
[2] *Chem. Zeit.*, 1905, **29**, 32.
[3] *Zeit. anal. Chem.*, 1900, **39**, 640.
[4] *Chem. Zeit.*, 1907, **31**, 537.

Substance	Acid value	Ester value	Saponification value	Ratio: $\frac{\text{ester value}}{\text{acid value}}$
Beeswax, unbleached	17–22	70–82	88–102	3.4–4.2
Beeswax, chemically bleached	19–25	69–74	95–99	2.7–3.2
Spermaceti	traces	....	121–135	....
Carnaüba wax	3–8	85.4[1]	79–88	29.4[1]
Chinese insect wax	traces	....	80–93	....
Japan wax	20–33	....	214–238	say 10
Myrtle wax	3	....	206–217	say 70
Tallow and "stearine"	say 2–12	....	193–198	say 15–97
Stearic acid (commercial)	200	nil	200	....
Colophony	180	10	190	....
Paraffin wax, ceresin, and ozokerite	nil	nil	nil	....
		[1]one sample		[1]one sample

Further investigation has shown that the "ratio-number" of genuine beeswax varies within wider limits than those stated by Hübl, but the range is still narrow enough to afford a valuable distinction between beeswax and the foreign fats and waxes likely to be added to it as adulterants. In the case of beeswax, the ratio-number is a true "constant"; but in the case of fats, such as Japan and myrtle "waxes," tallow, etc., the figures given in the table as ratio-numbers are accidental numbers depending upon the amount of free fatty acid in the sample, which may range from *nil* upward, and, therefore, the "ratio-numbers" of these fats will be higher the more nearly pure and neutral they are.

It is evident that the estimation of the ratio number alone will not suffice to detect adulteration in every case, as it is possible to prepare, without wax, mixtures having a normal ratio number. Thus, Lewkowitsch calculates that a mixture of Japan wax 37.5 parts, stearic acid 6.5 parts, and ceresin or paraffin wax 56 parts, will give the normal ratio number, 3.71. The examination must, therefore, be supplemented by other estimations; *e. g.*, iodine value, hydrogen liberated on heating with potassium hydroxide, estimation of the hydrocarbons, and other special tests.

The *iodine value* of genuine yellow beeswax ranges from about 7 to

14; bleached wax has a lower value, since bleaching destroys or modifies the iodine-absorbing substances. Adulteration with tallow or colophony would raise this value; paraffin or ceresin would lower it; Japan wax or carnaüba wax would be without effect. Beeswax could be largely adulterated without the normal iodine value being disturbed.

Japan wax and other *fatty substances* (*e. g.*, tallow, stearin, stearic acid) may be detected by boiling 1 grm. of the sample with 1.5 grm. of borax and 20 c.c. of water, when the aqueous liquid will become milky or gelatinous on cooling. With pure beeswax it remains clear or becomes but slightly turbid, and carnaüba wax and rosin behave similarly.

Japan and *myrtle wax* are denser than *beeswax*, and *tallow* and *stearin* somewhat lighter, but they all agree in having a notably lower fusing-point than pure beeswax, and much higher saponification values and "ratio-numbers"; they also yield *glycerol* on saponification. In doubtful cases, an estimation of the glycerol may be resorted to, when the amount found, multiplied by 10, gives the approximate weight of the adulterant. In 2 test mixtures of tallow and wax, containing, respectively, 50.9% and 28.4% of tallow, Benedikt and Zsigmondy found 4.93% and 3.00% of glycerol corresponding to 49.3% and 30% of tallow.

Free *stearic acid* is readily distinguished from the neutral fats and beeswax by its high acid value; in fact, in the absence of other adulterants, the percentage of stearic acid in a sample of wax might be approximately calculated from the acid value, taking that of beeswax as 20 and that of stearic acid as 200. As, however, the adulterant commonly used is a mixture of stearic acid, Japan wax, and ceresin, so proportioned as to give normal figures, a special test for stearic acid is required. The following modification of Fehling's test is recommended by Buchner: 3 grm. of the wax are boiled with 10 c.c. of 80% alcohol for a few minutes, and the tube is then immersed in cold water and shaken so that a thick paste results. After standing for 1 hour, the mixture is filtered, and the filtrate mixed with a large excess of water or with an alcoholic solution of lead acetate or calcium chloride, which make the test more sensitive. Normal waxes give only a faint opalescence, the cerotic acid dissolved by the boiling alcohol being almost entirely redeposited on cooling and standing, though after some hours they may show an amorphous deposit, especially soft African waxes.

Buchner regards a wax as genuine in this respect when it shows no deposit of stearic acid after 1 to 2 hours.

A quantitative modification of the test (making it applicable to rosin as well as fatty acid) has since been proposed by Buchner:[1] 5 grm. of the sample are treated with 100 c.c. of neutralised 80% alcohol, and the flask and contents are weighed. The alcohol is gently boiled for 5 minutes, with frequent agitation. The flask and contents are then cooled, and the solution made up to its original weight by the addition of 80% alcohol, well mixed, corked, and allowed to stand for 12 hours (*Berg*). The solution is then filtered through a ribbed filter, and 50 c.c. of the filtrate are titrated with N/10 potassium hydroxide with phenolphthaleïn. The figures thus obtained are known as *Buchner numbers*. Some results with waxes, fats, and mixtures, are given in the following table:

Substance	Buchner's number
Beeswax, yellow	3.6–3.9
Beeswax, white	3.7–4.1
Palm wax	1.7–1.8
Carnaüba wax	0.76–0.87
Japan wax	14.93–15.3
Stearin (from tallow)	1.1
Colophony	150.3
Stearic acid	65.8
Mixtures giving normal ratio numbers:	
1. Stearic acid, stearin and ceresin	21.40
2. Stearic acid, Japan wax and ceresin	17.80
3. Rosin, stearin and ceresin	22.00
Genuine beeswax + 25% mixture No. 1	8.42
Genuine beeswax + 50% mixture No. 1	11.30

According to Bohrisch and Richter,[2] the Buchner's number of genuine beeswax may range from 2 to 6. These authors, who fully examined 73 samples of beeswax from different parts of Germany, found 38 samples adulterated; of these, 34 contained paraffin and ceresin and 4 contained stearic acid, tallow or carnaüba wax.

Colophony or *rosin*, like stearic acid, if added to beeswax increases the acid value; and although the acid value of rosin is somewhat lower than that of stearic acid, its greater solubility in alcohol causes it to increase the Buchner number in greater proportion. Colophony is easily detected in beeswax by means of the *Liebermann-Storch reaction;* it may be estimated by applying Twichell's process to the mixture of rosin and fatty acids obtained by extracting the adulterated sample with boiling 80% alcohol and filtering when cold.

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[1] *Chem. Zeit.*, 1895, **19**, 1422.
[2] *Pharm. Centralh.*, 1906, **47**, 201, etc.

According to *Weinwurm*[1] 2 or 3% of ceresin or paraffin, or 5% of rosin, may be detected as follows: 5 grm. of filtered wax are saponified in 25 c.c. of N/2 alkali and the alcohol removed. 20 c.c. of glycerol are run in, the whole warmed in the water-bath till solution is effected, and 100 c.c. of boiling water added. Pure wax gives a clear, transparent, or translucent solution, through which ordinary printed matter may be read with ease. 5% of ceresin or rosin yields a cloudy liquid, and the print is no longer legible; 8% of ceresin causes a decided precipitate. If the solution be clear, 3%, or, if it be opaque, 2% of ceresin is added to another sample of the wax, and the saponification repeated, when from the appearance of the soap solution the presence or absence of either impurity may be deduced.

R. Henriques[2] reports favorably on the above process, but simplifies it by applying the Leffmann-Beam alkali-glycerol method for saponifying. A piece of wax about the size of a pea is boiled in a test-tube for 3 or 4 minutes with 5 c.c. of alkali glycerol (see p. 25). The solution, which is at first quite clear, becomes gradually cloudy. After boiling for about the time mentioned, the oil collects in a layer and the underlying fluid becomes clear. The bubbles of the boiling mass also now become smaller and the glycerol commences to distil. As soon as this point is reached the heating is discontinued. The fluid is now poured into another test-tube, in order to separate it from the unsaponified portion; an equal weight of hot water is added, and the liquid boiled and allowed to cool. In the case of pure wax the solution will be either quite clear and transparent, or at any rate sufficiently translucent to allow of large printed matter being read through it, as described by Weinwurm. Should, however, on the contrary, as much as 5% of foreign hydrocarbons be present, the fluid will be quite opaque. With an admixture of only 3% of ceresin or paraffin, the indication is uncertain, and the further treatment recommended by Weinwurm to meet such cases should be followed.

Lewkowitsch[3] states that he can recommend Weinwurm's test for pure beeswax, but that turbidity of the solution does not necessarily prove the presence of ceresin or paraffin wax, since it is also produced by carnaüba wax and insect wax.

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[1] *Analyst*, 1897, **22**, 242.
[2] *Ibid*, 1897, **22**, 292.
[3] Oils, Fats and Waxes, II, 772.

Paraffin, ceresin, and *ozokerite* are the only adulterants of beeswax which tend to reduce in a notable degree the saponification value. They also reduce the sp. gr. in a marked manner, but this indication has little more than a qualitative value. In a sample consisting solely of beeswax and hydrocarbon wax the proportion of the former may be deduced with considerable accuracy from the results of the saponification, each 0.1% of potassium hydroxide required representing 1.053% of beeswax in the sample.

Estimation of Fatty Alcohols and of Paraffin and Ceresin.—An adulteration of beeswax with less than 6% of ceresin or paraffin cannot be detected with certainty by any of the ordinary methods, because the relations between the free fatty acid and saponifiable and unsaponifiable matters in genuine beeswax vary within somewhat wide limits.

Werder[1] has proposed to saponify 2 grm. of the sample of wax with alcoholic potassium hydroxide, dry on sand, extract the dry mixture of soap, sand, etc., with pure dry ether in a Soxhlet extractor and weigh the mixture of alcohols and hydrocarbons. But as the residue of unsaponifiable matter obtained from 20 samples of genuine beeswax in this manner ranged from 48.55 to 53.01%, it is evident that at least 4.5% of paraffin wax or wax alcohols could be added to some samples without detection.

A preferable method is a direct estimation of the hydrocarbons present, and a method for doing this has been worked out by A. and P. Buisine,[2] based upon an observation of Dumas and Stas. The wax is saponified with potassium hydroxide and heated with potash lime, by which treatment the higher alcohols are converted into their corresponding fatty acids with evolution of hydrogen, the volume of which serves as a measure of their amount, while the hydrocarbons present are left unattacked and can be extracted from the residue with solvents. The following modification of the process has been described by Mangold:[3] 2 to 10 grm. of the wax are melted in a porcelain basin and intimately mixed, by stirring, with an equal weight of finely powdered caustic potash. The saponified mass, when cold, is powdered in a mortar, and intimately mixed with 3 grm. of a mixture (1 part potassium hydroxide, 2 parts lime) for every grm. of wax taken, it is then transferred to a thick-walled, pear-shaped bulb-tube, which is heated to 250° for 2 hours. An apparatus for conducting this operation is shown in the sketch. *A* is an iron vessel with a lid fastened down by screws and filled with mercury. The flask *E* is connected, gas-tight, with a Hofmann's burette, *H*, for measuring the hydrogen evolved. *T* is a thermometer and *V* a temperature regulator. *K* is a condensing tube for mercury vapour. It is advisable that the heating at 250° be continued for three hours to secure completion of the reaction, after which the flask is allowed to cool, and is broken up to liberate the residual mass, which is then powdered and extracted with petroleum spirit in a Soxhlet apparatus. The residue left on evaporation of the petroleum spirit is dried at 110° and weighed.

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[1] *Chem. Zeit.*, 1900, **24**, 967.
[2] *Bull. Soc. Chim.*, 1890, [3], **3**, 567.
[3] *Chem. Zeit.*, 1891, **15**, 799.

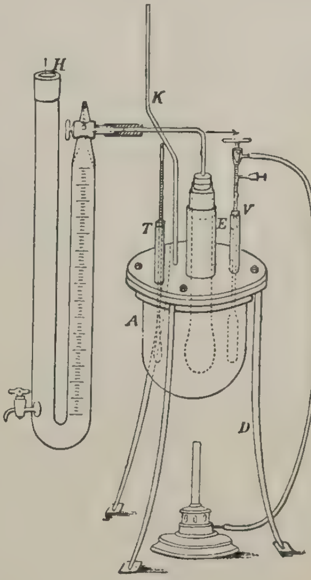

FIG. 8.

The following are some results obtained by A. and P. Buisine[1] in the examination of beeswax and adulterants:

	M. p., °	Acids soluble in water	Acid value	Saponification value	Iodine value	c. c. hydrogen from 1 grm. on treatment with KOH; 0° and 760 mm.	Hydro-carbons, %
Japan wax	47–54	2	18–28	216–222	6–7.55	69–71	0
China wax	53.5	2	22	218	6.85	72.3	0
Vegetable waxes	47–54	2	17–19	218–220	6.6–8.2	73–74	0
Carnaüba wax	83–84	0	4–6	79–82	7–9	73–76	1.6
Mineral waxes	60–80	0	0	0	0–0.6	0	100
Paraffins	38–74	0	0	0	1.7–3.1	0	100
Wax from "suint"	62–66	0	95–115	102–119	13–18.5	0	14–18
Waxy acids from "suint"	50–62	0	155–185	159–189	2.6–2.8	0	0
Suet	42–50.5	0	2.75–5	196–213	27–40	52–60	0
Stearic acid	55.5	0	204	209	4	0	0
Rosin	....	0	168	178	135.6	35	0
Yellow beeswax	62–64	0–1	19–21	91–97	8–11	53–57.5	12.5–14.5
Bleached beeswax	63–64	0–2	20–23	93–110 (?)	2–7	53–57	11–13.5

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[1] *Bull. Soc. Chim.*, 1891, [3], 5, 654.

If a measurement of the hydrogen is not required, the powdered mixture of saponified wax and alkali lime may be transferred to a simple boiling tube, which is closed by a rubber stopper and a short piece of bent glass tube, supported vertically in a bath of oil or melted carnaüba wax, and heated to 250° until no more gas is evolved; the temperature is then raised for a short time to 290°. Evolution of gas is ascertained by attaching a short length of rubber tubing to the glass tube and immersing the free end in water, but the rubber tube must not be left permanently attached, otherwise water may be sucked back and cause an explosion. When gas-evolution has ceased, the tube and contents are allowed to cool somewhat and the contents, while still hot, are removed as far as possible to a basin by means of a pointed glass rod. If allowed to become quite cold, the mixture sets hard and cannot be removed. The bottom of the boiling tube is finally broken out and what adheres to the sides scraped off as far as possible. The mixture is then placed in a paper extraction thimble with alternate layers of powdered pumice, the tube and basin are rinsed out with dry ether, which is poured through the thimble in the Soxhlet's tube, and the contents are then thoroughly extracted with dry ether for 4 or 5 hours. The (turbid) ethereal extract will contain a little soap. It is first shaken in a separating funnel with hydrochloric acid to decompose calcium soaps, and after drawing this off and washing with water it is shaken with dilute potassium hydroxide solution containing a little alcohol in order to remove fatty acids. After again washing with water, the ether is distilled off and the hydrocarbons weighed.

The proportion of hydrocarbons which has been found in genuine beeswax by Buisine, Mangold, Kebler, and Ahrens and Hett[1] has ranged from 11.0 to 17.5%. 15 samples of apparently genuine commercial yellow beeswax examined by Archbutt were found to contain from 12 to 16.7% of hydrocarbons; 6 obviously adulterated samples contained from 19.8 to 55.6%. The process is quite easy to work with a little practice, but is evidently not capable of detecting with certainty less than about 6% of hydrocarbons, owing to the comparative wide variation in the amount obtained from genuine samples.

Spermaceti is not usually an adulterant of beeswax, but occasionally its substitution will be profitable and may be practised. It is the only adulterant which would cause the sample to show less free acid, and yet require an increased proportion of alkali for its saponification, at the same time yielding glycerol and reducing the sp. gr. and m. p. In the absence of carnaüba wax, a direct indication of the presence and proportion of spermaceti may be obtained from an estimation of the m. p. of the higher alcohols of the sample.

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[1] *Zeit. öffentl. Chem.*, 5, 91.

From an inspection of the table on page 259, it appears that *carnaüba wax* requires for complete saponification a proportion of alkali not very different from that required by beeswax, but is distinguished from the latter by the smaller (but very variable) proportion of alkali required by the free acid. An admixture of carnaüba wax will be further indicated by the increased sp. gr. and higher m. p. of the sample.

Another proof of the presence of carnaüba wax is obtainable by removing free acid by alcohol and alcoholic potassium hydroxide, saponifying the separated neutral wax, precipitating the solution with lead acetate, and exhausting the precipitate with petroleum spirit, and decomposing the lead soap with hot hydrochloric acid. Beeswax, when thus treated, yields a product which is chiefly palmitic acid (m. p., 62°), while the product similarly obtained from carnaüba wax is largely cerotic acid (m. p., 79°).

Among the hydrocarbons isolated from the wax may be found unchanged *cholesterol*, if the sample had been adulterated with *wool wax*, since Lewkowitsch[1] has shown that cholesterol is practically unchanged by heating for 2 hours with soda-lime at 250°, and that of the total alcohols of wool wax 80% were recovered unchanged. In presence of wool wax, cholesterol may also be looked for in the unsaponifiable matter. Some results of examination of the unsaponifiable matter from waxes are given in the following table (Archbutt and Deeley):

	Unsaponifiable matter from		
	Beeswax	Carnaüba wax	Wool wax
Sp. gr. at $\frac{100°}{100°}$	0.8239	0.8426	0.957
M. p.	75°–76°	85°	44°–48°
Iodine value	....	....	35–40
Saponification value of mixed acetates	9.9–10.3	12.3	15.0–16.1

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[1] *J. Soc. Chem. Ind.*, 1896, 15, 14.

For the detection of *artificial colouring matters*, Lemaire[1] recommends the following tests:

A small fragment of the wax is dissolved in chloroform, and 2 or 3 drops of hydrochloric acid are added to the solution. The production of a rose-red colour indicates artificial colouring matter. Another portion is saponified by boiling with caustic soda solution, then treated hot with excess of hydrochloric acid. If a fugitive rose-red colour be obtained, which turns green on adding excess of ammonia, the wax is artificially coloured. Another piece of the wax is melted in a capsule with saturated boric acid solution; on evaporating to dryness the residue acquires a reddish colour with wax containing added colouring matter.

Dieterich[2] has shown that the analytical values of *beeswax from combs five years old* differed very little from those of new beeswax; the chief differences were in the colour, and the sp. gr. and m. p. of the waxes. Thus, the fresh wax was nearly colourless, had the highest sp. gr. (0.966) and the highest m. p. (65° to 66°). The old wax was dark brown, had the lowest sp. gr. (0.9599) and lowest m. p. (63° to 63.5°).

Hehner's Method for the Analysis of Complex Candle-mixtures.[3]—The estimation of the percentage of beeswax in so-called wax candles has assumed importance since, in 1904, the College of Rites of the Roman Catholic Church prescribed the use of candles containing definite percentages of beeswax for certain ritual and altar purposes. Such candles may contain, besides beeswax, paraffin (ceresine, ozokerite), stearine (commercial stearic acid), and spermaceti.

Hehner's method for the analysis of such mixtures depends primarily upon the approximate constancy of composition of normal beeswax. Thus, 24 samples of good commercial bleached wax were found by Hehner to contain free acid, calculated as cerotic acid[4] ranging from 15.5 to 17.6% and averaging 16.6% or almost exactly one-sixth of the wax, and saponifiable esters, calculated as myricyl palmitate, ranging from 85.2 to 89.9% and averaging 87.7% or very nearly 5.3 times the acidity expressed as above. The free acid extracted from a small number of samples was found to have a molecular weight of 407 ($C_{27}H_{54}O_2 = 410$).

Upon the basis of these figures, the composition of a mixture containing only *beeswax* and *paraffin* is easily inferred from the depression in acidity and saponifiable substance, the relation between these (1:5.3) remaining unaltered. With a mixture of *beeswax* and *stearine* the amount of saponifiable matter gives the measure of the wax, and by difference that of the stearine, commercial stearine as used for candle manufacture having an average molecular weight of about 272. Lastly, in a mixture of *beeswax* and *spermaceti* the free acid measures the amount of wax, the spermaceti being practically free from acid. It is when the ingredients are unknown, or when the ratio is disturbed in two directions by the presence of both stearine and spermaceti that the problem becomes difficult; an estimation of one or both of the main components of beeswax then becomes essential.

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[1] *J. Soc. Chem. Ind.*, 1904, **23**, 840.
[2] *Chem. Zeit.*, 1907, **31**, 987.
[3] From a paper by Otto Hehner read before the Society of Pubic Analysts.
[4] Brodie's formula, $C_{27}H_{54}O_2$.

Except carnauba wax, which is not commonly used in candle manufacture, beeswax is the only candle material which contains free cerotic acid, but for the separation of this acid from the esters Hehner points out that alcohol cannot be used, since the esters themselves are much too soluble in alcohol for even an approximate estimation to be based upon the greater solubility of the free acid. He therefore converts the free acid into potassium salt, which is soluble in warm water and from which the insoluble esters can be separated by shaking out with ether. The difficulties of the process are mechanical and arise chiefly from the great viscosity of the soap solution. Thus, with pure beeswax not more than 5 grm. can be dealt with in a volume of 1500 to 2000 c.c., but with mixtures the mechanical difficulties become less. The process is carried out as follows:

10–12 grm. of the material to be examined are boiled with 70–100 c.c. of alcohol and carefully and exactly neutralised by adding phenolphthalein and alcoholic potassium hydroxide solution; about 600 c.c. of hot distilled water are then added and the unsaponified matter is allowed to come to the top, where it forms an oily layer. The soapy turbid solution is siphoned from below the oily layer into a large separating funnel holding about 2000 c.c., the layer being washed 3 times more with hot water, so that the total volume of soapy liquor in the funnel, containing the whole of the originally-free acid, measures about 1500 c.c. (The unsaponified portion can be kept for subsequent operations.) The soapy liquor is cooled to about 35°, and to it are added from 150 to 200 c.c. of ether and the funnel very gently shaken. Violent shaking must on no account be resorted to, as an emulsion would form with which it is almost impossible to deal. The funnel is placed in a large vessel of water at about 35° and left for an hour or two for the ether to rise. The aqueous portion is then drawn off into another funnel and shaken twice more with ether, after which it should be clear or nearly so. Alcohol must not be added at this stage to promote separation of the ether, as partial saponification of the esters would occur and lead to inaccurate results. The ethereal solution is rejected as it is separated, and *not* washed with water. To the soap solution is now added hydrochloric acid in excess, by which the soap is decomposed and a layer of ether containing the liberated fatty acid rises. This is allowed to separate thoroughly, and the lower aqueous layer is drawn off and rejected. The fatty ether, having been washed carefully with hot water several times, is evaporated, and the residual fatty acids dried and accurately weighed; they are then very carefully titrated with alcoholic potassium hydroxide solution, which must not be stronger than N/3, owing to the high molecular weight of the cerotic acid. Care must also be taken that the alcohol in which the acid is dissolved before titration is exactly neutralised and that the alkaline solution is kept free from carbonate and accurately standardised.

The only acids which can compose the material titrated are the free acids of the wax, with a mean molecular weight of about 407, and the "stearine," with a molecular weight of 272 ± 1. The molecular weight gives, therefore, the proportion of crude cerotic acid in the mixture.

In a separate portion of the original wax mixture the total acidity is now estimated as usual, and also the ester value. The molecular weight of the free acids being known, the actual percentage of free acids in the mixture can be calculated, and as the percentage of real wax acid of molecular weight 407 in these free acids is also known, the percentage of free wax acid in the mixture can also be calculated. Multiplying this by 6, the amount of beeswax in the mixture is arrived at; and subtracting it from the total acid, the percentage of "stearine" is obtained. Multiplying the wax acid by 5.3, the ester portion of the beeswax, expressed in terms of myricine, results; this subtracted from the total saponifiable matter gives the measure of any spermaceti that may have been present. A calculation reducing this remainder from terms of myricine, with an equivalent of 676, into terms of spermaceti, with an equivalent of about 480, results in a close approximation of the actual percentage of spermaceti. This remainder, if any, is paraffin. The presence of paraffin, if more than 4 or 5%, is always seen during the saponification for the estimation of the ester value. The paraffin is the only material estimated by difference.

Of other acid substances which would interfere with the process there might be present traces of mineral or oxalic acid from the bleaching processes. These can easily be tested for and, if necessary, removed by melting some of the substance with boiling water and testing the aqueous solution. Resin acids do not mix to any practicable amount with candle materials. The bee stops all crevices of the hive with various resins collected from trees and buds, called *propolis.* All honeycomb is more or less contaminated with propolis, but the latter separates from the molten wax and is not an ingredient of commercial wax. Carnauba wax has an exceedingly small acid value, which need not be taken into consideration.

The following results of analyses of known mixtures show the degree of accuracy obtainable:

	Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found
Beeswax.......	48	50	80	85	20	18	69.8	65	26.5	28
Spermaceti.....	4	4	0	0	10	12	14.0	15	.....	.....
Stearine.......	10	10	10	10	35	36	6.3	10	.....	.....
Paraffin........	10	36	10	5	35	34	9.9	10	.....	.....
Ceresin........	28									

When the candle mixture is free from spermaceti the total saponifiable matter, calculated as myricine, should be 5.3 times the amount of wax acid found. How nearly this is the case is shown by the following analyses of candle material acknowledged to be free from spermaceti:

ANALYSES OF CANDLES FREE FROM SPERMACETI.

Total free acid calculated as $C_{27}H_{54}O_2$	Real wax acid of molecular weight 407	Real percentage of free acid	Total saponifiable esters calculated as myricine	Paraffin	Wax acid × 6	% wax stamped on candle
25.7	12.5	22.4	66.0	present	75	75
22.1	11.1	19.2	55.3	present	66.6	65
55.3	3.1	39.4	16.6	present	18.6	25
25.6	12.4	22.1	64.3	present	74.4	75
22.1	10.6	19.1	56.5	present	63.6	65
55.4	3.3	39.6	17.6	present	19.8	25
23.4	10.8	20.6	55.4	present	64.8	65
50.9	3.2	36.9	16.4	present	19.2	25
25.9	12.6	22.4	64.8	present	75.6	75
23.3	11.2	19.4	55.3	present	67.2	65
51.5	4.4	37.3	22.4	present	26.4	25
23.7	9.4	19.8	47.5	present	56.4	75
50.9	1.9	36.1	9.9	present	11.4	25
73.7	nil	50.0	1.3	present	0	25
30.3	9.0	44.8	46.4	present	54.0	65
50.3	2.8	35.8	23.5	present	16.8	75
34.1	3.6	38.8	26.8	present	21.6	75
26.8	12.4	23.0	67.2	present	74.4	75
49.1	3.9	35.6	23.3	present	23.4	75

In all these cases, the free acid in column 1 multiplied by 5.3 equals or exceeds the total saponifiable as myricine and leaves no room for spermaceti or fatty substance, satisfactorily proving that the real wax acid had been correctly estimated, that spermaceti was absent, and that the wax used had been of normal composition and not Bombay or other abnormally composed wax. Some of the stamped percentages were fully confirmed by the analysis, in other cases the stamp was obviously deceptive. From the figures in the table the real composition of the candles can be calculated, as already explained. The following are analyses of material containing spermaceti:

ANALYSES OF CANDLES CONTAINING SPERMACETI.

Analytical Data.					
Total free acid calculated as $C_{27}H_{54}O_2$	34.8	10.9	14.8	34.9	59.1
Actual wax acid	9.6	10.9	12.3	9.1	4.0
Real percentage of free acid	27.5	10.9	14.2	27.6	42.3
Total saponifiable esters calculated as myricine.	63.4	64.7	74.8	62.0	30.6
Calculated Composition.					
Beeswax	57.6	65.4	73.8	54.6	24.0
Spermaceti	8.8	4.8	8.1	9.7	6.6
Stearine	17.9	none	2.5	18.5	38.3
Paraffin	15.7	29.8	15.6	17.2	31.1
% of wax stamped on candle	55	65	75	55	25

Hehner points out that his method is not applicable to candle mixtures containing abnormal or insect waxes (see Ghedda Wax) which he does not regard as true beeswax. For the analysis of mixtures which may contain such waxes besides the four main ingredients above mentioned, the alcoholic as well as the acid constituents need examination. No satisfactory method is at present available. Hehner has endeavored to elaborate a method based upon the fact that oxidation by chromic acid in acetic acid solution converts a wax alcohol, such as cetylic, into the corresponding acid, but in practice the action is complicated by the fact that partial acetylation of the alcohol occurs and the acetyl derivative is not attacked by the chromic acid. The application of the method to a comparatively simple wax-like spermaceti and the estimation of paraffin in admixture with spermaceti or sperm oil is illustrated as follows:

The substance is saponified, diluted, and the paraffin and wax alcohols shaken out with ether. The fatty acids are liberated from the soap solution and their mean molecular weight and iodine value determined, from which the proportions of palmitic, stearic, and oleic acids are deducible. The alcohols + paraffin are dissolved in glacial acetic acid and solid chromic acid is introduced, in small quantities at a time, until a decided excess is shown by the colour of the liquid. The solution is largely diluted with hot water, whereby all reaction products and the paraffin separate. These products are boiled with excess of alcoholic potassium hydroxide to hydrolyse the acetyl derivatives formed, and by addition of water and acid separation of the material from the alcohol is again effected. Once more oxidation with chromic acid in glacial acetic acid is carried out, and practically the whole of the wax alcohol will now have been converted into its corresponding fatty acid. By treatment with alcoholic potassium hydroxide, dilution of the soap solution and shaking out with ether, a separation of the paraffin is effected, while the fatty acid is separated from the soap solution and its molecular weight ascertained. An insight into both the acid and the wax-alcoholic portions of the substance is thus obtained, and any paraffin present is separated and estimated.

The same process is applicable to more complex mixtures; but there are many practical difficulties caused by the sparing solubility of myricyl alcohol in ether and the fact that the soaps of the higher acids are so little soluble in water and form such very viscid solutions. Further investigation of this process is proceeding in Hehner's laboratory.

Indian Beeswax (Ghedda Wax).

Chinese Beeswax.

This wax, though of good quality and colour, yields analytical values which differ very materially from those obtained with European waxes. It is softer and more plastic than normal beeswax. The acid values are very low, and the ester values high, with the result that the ratio-numbers range from 7.4 to 17.9, the mean being about 12.

According to Hooper,[1] Ghedda wax is derived from three species of bees, *Apis dorsata*, *A. indica*, and *A. florea*, but chiefly from *A. dorsata*. The analytical characters of the waxes are shown in the following table:

Origin of wax		M. p., °	Acid value	Saponification value	Ester value	Iodine value
A. dorsata (23 samples)	Max.	67.0	10.2	105.0	97.8	9.9
	Min.	60.0	4.4	75.6	69.5	4.8
	Av.	63.1	7.0	96.2	89.4	6.7
A. indica (7 samples)	Max.	64.0	8.8	102.5	95.9	9.2
	Min.	62.0	5.0	90.0	84.0	5.3
	Av.	63.25	6.8	96.2	89.6	7.4
A. florea (5 samples)	Max.	68.0	8.9	130.5	123.8	11.4
	Min.	63.0	6.1	88.5	80.8	6.0
	Av.	64.2	7.5	103.2	95.6	8.0

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[1] *Indian Agric. Ledger*, 1904, 73–100; *J. Soc. Chem. Ind.*, 1904, 23, 828.

Buchner[1] is of opinion that Ghedda wax is a true beeswax, differing from the European kind quantitatively but not qualitatively. Thus, he obtained by analysis of a sample, cerotic acid, 5.13; palmitic acid, 37.87; melissyl alcohol, calculated from the hydrogen evolved in Buisine's process, 65.09; hydrocarbons, 8.65. Hooper says Indian wax is rarely adulterated, and as there is a large quantity of it produced, analysts must be on their guard against mistaking specimens of this wax for adulterated beeswax.

Buchner[2] obtained the following results by examination of several samples of Indian and Chinese beeswax.

Kind of wax	M. p.,°	Acid value	Saponification value	Ester value	Ratio number	Iodine value
Indian........	65	6.1	83.3	77.2	12.1	10
Indian........	66	6.01	82.12	76.11	12.6	10
Chinese.......	66	7.55	93.7	86.15	11.4	..
Chinese.......	.....	6.28	90.2	83.82	13.9	..
Chinese.......	.....	6.40	96.7	90.30	15.6	..
Chinese.......	62–63	5.33	95.61	90.28	17.9	..
Chinese.......	.....	8.72	120.17	111.45	12.78	..
Chinese.......	.....	7.51	92.14	84.63	11.26	..
Chinese.......	.....	9.74	117.40	107.66	11.06	..

Hooper (*loc. cit.* above) also describes the wax produced by the Dammar or Kota bees, *Melipona* (*Trigona*) species. These very small stingless insects produce a sticky, dark coloured wax, having a m. p. of 70.5°; acid value, 20.8; saponification value, 110.4; ester value, 89.6; ratio number, 4.3; and iodine value, 42.2. The product more nearly resembles the propolis of honey bees than true wax, from which it differs largely in chemical and physical characters.

Very similar to Indian beeswax from A. dorsata is *Annamese beeswax*, which has been examined by Bellier.[3] The commercial wax is grayish-yellow, not homogeneous, and appears to have been kneaded by hand into prismatic cakes which were found to contain 5.02% water, 0.5% insoluble in benzene, and 0.08% of ash. After melting and straining, it resembles European beeswax in general appearance, but its chemical and physical characters are similar to those of the Indian wax, as shown below.

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[1] *Chem. Zeit.*, 1905, **29**, 32, and 1906, **30**, 528.
[2] *Zeit. öffentl. Chem.*, **3**, 570.
[3] *Ann. Chim. anal. appl.*, 1906, **11**, 366.

Sp. gr.	0.964
M.p.	61°
Acid value	7.8
Saponification value	94.4
Ester value	86.6
Ratio number	11
Iodine value	6
Hydrogen liberated at 250° by potassa lime, per grm. of wax	60.3 c.c. at 0° and 760 mm.
Hydrocarbons	10.5

CARNAUBA WAX. CARNAHUBA WAX.

(See pp. 73, 261 and 272.) This is a very hard, sulphur-yellow or yellowish-green substance, which coats the leaves of a palm, *Copernicia cerifera*, the carnaüba tree of Brazil. The leaves are detached, beaten, and the dust, amounting to about 50 gr. per leaf, collected and melted into a mass. The brittle, lustrous wax thus obtained has a sp. gr. of 0.999, melts at 84° to 85°, and dissolves in alcohol and boiling ether. On ignition, it leaves a small quantity of ash, which often contains iron oxide.

Carnaüba wax has a very complex composition. It has been investigated by Bérard, Story-Maskelyne, Piverling, and very thoroughly by Stürcke,[1] who found it to consist mainly of myricyl cerotate. In the alcoholic extract of the wax, Bérard found free cerotic acid, since confirmed by Hehner and Hübl; Story-Maskelyne and Stürcke, in the same solution, found free myricyl alcohol. Stürcke obtained from carnaüba wax the following substances: a crystalline *paraffinoid hydrocarbon* melting at about 59°; *ceryl alcohol*, $C_{27}H_{55}OH$, a crystalline substance melting at 76°; these two fractions did not exceed 1 1/2 to 2%. *Myricyl alcohol* was found to the extent of about 45%; a *dihydric alcohol*, $C_{23}H_{46}(CH_2OH)_2$, melting at 103.5°, and converted on heating with soda-lime into an acid melting at 102.5°, and having the composition, $C_{23}H_{46}(COOH)_2$; an *acid* of the formula $C_{23}H_{47}.COOH$, melting at 72.5°, isomeric with lignoceric acid; *cerotic acid*, the chief acid of carnaüba wax, melting at 79°, or an acid isomeric therewith; a *hydroxyacid* of the formula $CH_2OH.C_{19}H_{38}.COOH$, yielding on heating with soda lime the acid $C_{19}H_{38}(COOH)_2$, melting at 90°.

Allen and Thomson[2] obtained 54.87%, and Archbutt 52.4% of unsaponifiable matter (alcohols, etc.) from carnaüba wax. Lewkowitsch[1] found the acetyl value 55.24, the same sample having a saponification value of 79.68.

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[1] *Annalen*, **223**, 283.

[2] *Chem. News*, 1881, **43**, 267.

The constants of carnaüba wax have recently been redetermined by Radcliffe.[2]

A sample of Cearà wax melting at 84°, was used for the experiments; and also a bleached sample, which melted at 61°. The figures for the acid value range from 4 to 8, and O. Eichhorn[3] states that by dissolving 3 grm. of the wax in 120 c.c. of boiling amyl alcohol he obtained an acid value of 9.71. A repetition of the above method gave for the Cearà wax 5, and for the bleached sample 0.56. The saponification values stated by various observers vary from 79 to 95. A series of experiments were made, in order to ascertain which method gave the maximum value; and it was found that, by treating 5 grm. of the wax with 60 c.c. of amyl alcohol and 50 c.c. of ordinary alcoholic potassium hydroxide (60 grm. to the litre) and boiling for 6 hours, the figure 88.3 was obtained, the bleached sample giving 33 to 34. The iodine value by Wijs' method was, after 24 hours, 13.17%. The values obtained on one and the same sample of carnaüba wax were:

M. p. (in capillary tube)	84°
Acid value	2.9
Saponification value	88.3
Ester value	85.4
Iodine value	13.17

Carnaüba wax when in a separate state is readily recognised by its physical characters and the results of its saponification. It is sometimes employed as an adulterant of beeswax, in which its presence may be recognised by the high sp. gr. and m. p. of the substance, and by the m. p. of the fatty acids produced by the saponification of the neutral esters of the sample. The presence of carnaüba wax in soap is best recognised by mixing the sample with sand, drying thoroughly, and exhausting the mixture with petroleum spirit (boiling at about 100°) or hot toluene in a Soxhlet's tube. The residue left on distilling off the solvent is identified by a comparison of its characters with those of the unsaponifiable matter from carnaüba wax given on p. 261, or by the isolation of myricyl alcohol. The weight of alcohols, etc., divided by 0.53 gives approximately the amount of carnaüba wax in the quantity of soap employed.

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[1] *Analyst*, 1899, **24**, 321.
[2] *J. Soc. Chem. Ind.*, 1906, **25**, 158.
[3] *Zeit. anal. Chem.*, 1900, **39**, 640.

E. Valenta has found carnaüba wax in a number of commercial ceresins and paraffins which were characterised by their high m. p. and great hardness. It is employed to impart these properties and to give a peculiar lustre to the wax. Valenta gives the following figures showing the influence of carnaüba wax, melting at 85°, on the m. p. of mixtures containing it.

Percentage of carnaüba wax	M. p.,° of substance or mixture		
	With stearic acid	With ceresin	With paraffin wax
0	58.50	72.10	60.15
5	69.75	79.10	73.90
10	73.75	80.56	79.20
15	74.55	81.60	81.10
20	75.20	82.53	81.50
25	75.80	82.95	81.75

These results show a very marked increase in the m. p. of the substances by the addition even of 5% of carnaüba wax. Further additions increase the m. p. in a diminished ratio.

The proportion of carnaüba wax existing in admixture with the foregoing substances, or with Japan wax, can be ascertained by estimating the percentage of potash required for the neutralisation of the free acid and for the saponification of the esters of the sample, and by the estimation of the unsaponifiable matter.

Carnaüba wax is bleached for candle-making[1] by filtration through animal charcoal, or by hydrogen peroxide or potassium bichromate. Candles are seldom made of carnaüba wax alone, but of a mixture containing 20 to 30% of stearine and ozokerite. "Brilliant paraffin" is a mixture of paraffin wax, 75%; carnaüba wax, 25%. "Brilliant gelatin," used for finishing leather, is prepared by adding a liquid containing water, potassium carbonate, and carnaüba wax to a solution of gelatin. Carnaüba wax is also used in making special varnishes, and in the manufacture of phonograph cylinders.

CHINESE INSECT WAX.

(See p. 73.) In Western China,[2] not far from the Thibetan frontier, an evergreen tree, *Ligustrum lucidum*, grows. Early in the spring, numerous brown pea-shaped scales containing the larvæ of the wax insect, *Coccus pela*, appear on its boughs and twigs. These scales are gathered, wrapped in packages, conveyed about 200 miles to Chia-ting, the centre of the industry, made up into small packets with leaves, and suspended under the branches of a species of ash. The insects on emerging from the packets creep up to the leaves of the ash trees, and afterward descend to the twigs and branches on which the wax is deposited by the males. After 100 days, the deposit is complete, and the branches are then cut down, the wax scraped off, and what remains on the twigs is separated by boiling with water, which destroys the insects and necessitates a fresh supply of larvæ in the next year from outside districts. A pound of larvæ scales will produce 4 or 5 pounds of wax.

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[1] *J. Soc. Chem. Ind.*, 1894, **13**, 744.

[2] *J. Soc. Chem. Ind.*, 1892, **11**, 282.

The product is a clear white, highly crystalline, brittle wax, called from its appearance "vegetable spermaceti." It consists, principally, of ceryl cerotate. It is chiefly used in China for coating the exteriors of candles made of animal and vegetable tallow, also as a sizing for paper and cotton goods, for imparting a gloss to silk, and as a furniture polish.[1]

SPERMACETI.

(See also table on p. 73.) Spermaceti exists in solution in the oil from the sperm whale, bottlenose whale, dolphin, and allied cetaceans, but not in the oil from the whalebone whales. It is present most abundantly in the oil from the head cavities, and is commonly stated to be a special product thereof. This is an error, the oil from the blubber also depositing spermaceti on cooling, and in practice the head and blubber oils are treated together.

Crude spermaceti forms crystalline scales of a yellowish or brownish colour. It is purified by fusion, pressure, and boiling with a solution of potash, to remove adhering oil and neutralise traces of acid. In practice, the complete removal of the oil is not aimed at, as a small proportion is found to confer desirable properties on the product. It is then remelted and cast into cakes.

As thus obtained, spermaceti is a snow-white or transparent substance of marked crystalline structure. It fuses at 43° to 49°.[2] The sp. gr. at the ordinary temperature is commonly between 0.942 and 0.946; but differing statements are made, probably owing to difficulty attending the estimation, in consequence of the crystalline structure of the substance. Much more trustworthy estimations can be made of the sp. gr. in the molten condition, which ranges between 0.808 and 0.816 at a temperature of 98° to 99° (water at 15.5°=1.0).

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[1] *J. Soc. Chem. Ind.*, 1897, **16**, 685.

[2] The figure commonly stated as the m. p. of spermaceti really refers to the solidifying-point as determined by the titer test. The spermaceti from bottlenose oil melts at a sensibly higher temperature than that from true sperm oil.

Spermaceti is insoluble in water, but dissolves in boiling alcohol, ether, chloroform, carbon disulphide, and fixed and volatile oils. Cold alcohol dissolves the adhering oil only. From its solution in hot alcohol or ether it separates in crystalline form, and, after repeated purification in this manner, the m. p. reaches to 53.5°, and the crystals consist of pure cetin.

Cetin or Cetyl Palmitate, $C_{16}H_{33}.O.C_{16}H_{31}O$, is the chief constituent of spermaceti, which, in addition, contains certain homologous ethers. Thus, on saponification it yields:

Acids		Alcohols	
Lauric	$C_{12}H_{24}O_2$	Dodecyl alcohol	$C_{12}H_{26}O$
Myristic	$C_{14}H_{28}O_2$	Tetradecyl alcohol	$C_{14}H_{30}O$
Palmitic	$C_{16}H_{32}O_2$	Cetyl alcohol	$C_{16}H_{34}O_2$
Stearic	$C_{18}H_{36}O_2$	Octadecyl alcohol	$C_{18}H_{38}O_2$

Cetyl Alcohol, $C_{16}H_{33}.OH$, may be obtained in a state of approximate purity by saponifying spermaceti previously crystallised from hot alcohol. On evaporation of its ethereal solution, cetyl alcohol remains as a white or yellowish-white, tasteless, inodorous, crystalline mass, melting at 49.5°. When carefully heated it distils without decomposition at about 400°, and is volatile with the vapour of water. It is quite insoluble in water, but readily soluble in alcohol, ether, and petroleum spirit.

When heated with potash-lime to a temperature of 250°–280°, cetyl alcohol is converted into potassium palmitate, with evolution of hydrogen.

Cetyl alcohol heated with glacial acetic acid forms cetyl acetate, $C_{16}H_{33}.C_2H_3O_2$, a crystalline substance melting at 22° to 23°, and boiling at 200° under a pressure of 15 mm.

The proportion of potassium hydroxide required for the saponification of spermaceti is about 12.8%, corresponding to a saponification-equivalent of 438. The molecular weight of cetyl palmitate is 480, and hence these figures point to the presence of a notable proportion of lower homologues of palmitic acid, such as have been proved by other means to exist in spermaceti.

On saponification, agitation of the aqueous solution of the resultant soap with ether, and subsequent decomposition of the soap solution with an acid, Allen found a sample of spermaceti to yield:

Higher alcohols, melting at 47.5°	51.48%
Fatty acids, mean combining weight, 231.4	52.96%

Pure cetyl palmitate would yield, theoretically:

Cetyl alcohol, melting at 49.5°	50.41%
Palmitic acid, combining weight, 256	53.33%

Commercial Spermaceti.—Spermaceti is liable to turn yellow and rancid on exposure to air. Hehner found 2 out of 3 samples to be wholly devoid of free acid, while the third had an acidity corresponding to 0.81% of free palmitic acid. 12 samples examined by Kebler[1] ranged in acid value from 0.09 to 0.47 (=0.04 to 0.21% of palmitic acid) and in saponification value from 124.8 to 136.3. Five specimens of genuine spermaceti examined by Dunlop[2] gave the following results:

Sample number	1	2	3	4	5
Description	Spermaceti from "head-matter" of Cachalot; extracted in laboratory.		Refined spermaceti from a reliable source		
M. p., °	41–41.5	41–42	44–44.5	44.5–46	45–45.5
Solidifying-point, °	41		44	45.7	45
Iodine value (Wijs)		9.33	7.21	5.32	5.50
Saponification value	129.0	129.0	120.6	121.8	120.6
Wax alcohols, etc., %	54.22	53.20	53.00	51.56	
Fatty acids, %	49.78		50.58		
Free (oleic) acid, %				0.10	0.24
M. p. of fatty acids	32–33		39.5–40		
M. p. of wax alcohols, etc.	46–46.5	45.5–46	47–47.5	47.5–48	47.5–48
Iodine value of wax alcohols, etc.		6.35	4.26	3.41	2.98

Dunlop directs attention to the iodine values found by him, which are considerably higher than those hitherto recorded. Pure spermaceti absorbs no iodine. Lewkowitsch found commercial samples of the wax absorbed from 3.52 to 4.09%, due, probably, to small amounts of sperm oil adhering to the spermaceti. In the case of Dunlop's No. 2

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[1] *Rev. intern. falsif.*, **10**, 208; *J. Soc. Chem. Ind.*, 1898, **17**, 383.
[2] *J. Soc. Chem. Ind.*, 1908, **27**, 63.

sample, the exceptionally high iodine value is accounted for by the presence of more sperm oil than usual, owing to the low temperature and pressure employed in its preparation.

The behaviour on saponification, low acid and iodine values, together with its physical characters, amply suffice to identify spermaceti and to detect any admixture. The most likely adulterants are stearic and palmitic acids, stearin, tallow, and paraffin wax.

Palmitic and *stearic acid* will be detected and determined by estimating the free acid of the sample by titration with standard alkali and phenolphthaleïn, any proportion of acid less than 1% being neglected. An admixture of beeswax would somewhat increase the acidity of the sample. Added fatty acids may also be detected by melting the sample in a test-tube immersed in boiling water, agitating with 2 volumes of ammonia of 0.960 sp. gr., and allowing the whole to cool. If the spermaceti be pure, it will rise to the surface and leave the ammonia nearly or entirely clear; but if adulterated with stearic acid, a thick white emulsion will be formed, which retains the spermaceti if the proportion of the adulterant be large, but allows it to rise and form a separate layer if the stearic acid is present only in moderate amount. 1% of the adulterant is said to be recognisable by this test. Dunlop found it reliable, down to about 3%, but with smaller quantities the test appeared somewhat uncertain.

Tallow and *stearin* are recognisable in spermaceti by the iodine value being in excess of the numbers given above; by the change in the fracture, feel, and appearance of the sample; and by the tallowy smell produced on heating. They will also be indicated by the results of the saponification of the sample. In presence of either adulterant the percentage of alkali required for saponification will be increased, the saponification-equivalent correspondingly lowered, while the ether-extract will be diminished and the percentage of fatty acids increased almost in direct proportion to the extent of the adulteration. The saponification-equivalent of spermaceti averaging about 438 and that of tallow about 288, each unit per cent. of the adulterant will reduce the saponification-equivalent by 1.5. Thus, if a sample be found to require 14.78% of potassium hydroxide for saponification, corresponding to an equivalent of 380, the proportion of tallow may be assumed to be

$$\frac{(438-380)\times 2}{3}=38.7\%$$

If free fatty acids are present, together with neutral fats, the same method of calculation will show approximately the sum of the two adulterants and, the fatty acids having been previously estimated, the proportion of fats can be ascertained; or, preferably, the fatty acids may be previously estimated in the same portion of the sample, and only the additional quantity of alkali required for the saponification of the neutral fat taken into account in the calculation. The ether-residue from genuine spermaceti being at least 50%, and from fatty acids and neutral fats practically *nil*, the percentage of such adulterants can be ascertained with accuracy. Each unit % of ether-residue obtained, represents approximately, 2% of real spermaceti in the sample.

Paraffin diminishes notably the sp. gr. of the sample, yields 100% of ether-residue, neutralises no alkali, and cannot, by admixture with any proportion of fatty acid or fat, be made to give results on saponification similar to those yielded by genuine spermaceti. Thus, a mixture of equal parts of paraffin and tallow will yield 50% of ether-residue, but the saponification-equivalent will be about 576. Paraffin can be detected by Holde's test, as in the case of sperm oil, as little as 3.5% being capable of detection according to Dunlop. Smaller quantities may, however, be detected by boiling the unsaponifiable matter with acetic anhydride and observing the behaviour of the solution. If the spermaceti is genuine, the solution remains clear on cooling, but if paraffin wax is present, it becomes turbid, owing to separation of the latter. As little as 1% of paraffin wax in spermaceti can be detected in this manner (Dunlop).

BUTTER FAT.

By CECIL REVIS, A. C. G. I., AND E. R. BOLTON.

(See p. 72.) Butter fat is the fat of milk. When used without qualification the term means the fat from cow's milk, but the milks of other animals yield similar products.

Butter fat, as obtained from butter, has the well-known colour, taste, and smell of butter itself. The melting and solidifying points differ considerably in different samples, being influenced by the mode of feeding and other factors. According to Meyer (*Milch Zeit.*, 1892, 21, 49) the m. p. is lowered by food consisting of easily digestible carbohydrates, but raised by straw, oil cakes, and sour fodder. Bell states that the m. p. is usually comprised between 29.5° and 33°, the maximum being 34.7°. These figures are in agreement with those of other observers. The sp. gr. and the coefficient of expansion are higher than those of most of the fats likely to be used for adulteration.

Butter (save for small quantities of unsaponifiable matter, discussed later) is composed almost exclusively of triglycerides of the fatty acids. The characteristic constituent is the radicle of butyric acid, which is present together with certain of its higher homologues.

Bell obtained the following products by saponifying 100 parts of butter fat.

Butyric acid	6.13	
Caproic, caprylic and capric acids	2.09	(mean combining weight = 136)
Myristic, palmitic, and stearic acids	49.46	= 85.56
Oleic acid	36.10	
Glycerol (calculated)	12.54	
	106.32	

The fatty acids soluble in water were regarded as butyric acid. Those soluble in hot water only appear in the analysis as caproic acid, etc., the combining weight being deduced from the amount of barium carbonate left on igniting the salts.

Browne (*J. Amer. Chem. Soc.*, 1899, **21**, 807) gives the following composition:

Acid	Percentage of acid	Percentage of triglycerides
Dihydroxystearic	1.00	1.04
Oleic	32.50	33.95
Stearic	1.83	1.91
Palmitic	38.61	40.51
Myristic	9.89	10.44
Lauric	2.57	2.73
Capric	0.32	0.34
Caprylic	0.49	0.53
Caproic	2.09	2.32
Butyric	5.45	6.23
Total	94.75	100.00

According to Duclaux (*Compt. rend.*, 1886, **102**, 1022), butter fat contains from 2 to 2.26% of caproic and from 3.38 to 3.65% of butyric acid.

Lewkowitsch (Oils, Fats and Waxes, 4th Ed., 668) only finds 0.49% of stearic acid in the insoluble fatty acids of a butter fat giving a Reichert-Meissl value of 28.1. Hehner and Mitchell also found very small proportions of stearic acid, and in some cases none. Some observers have found amounts over 6% but in view of the above, these results must be accepted with reserve. James Bell (*The Chemistry of Foods*, 2, 44) designated a mixed ester found by him as glyceryl palmito-butyrate; A. W. Blyth and Robertson (*Proc. Chem. Soc.*, 1886, 5), designated an ester examined by them as glyceryl stearo-palmito-butyrate.

Examination of Butter Fat.—The examination of butter fat is undertaken for the purpose of detecting adulteration with foreign fats. Many substances have been described as being used for such purpose, but the fats used are practically confined to lard, oleo products, and coconut oil. Cottonseed oil, stiffened with beef stearin, and cottonseed stearin, and other vegetable oils are also used, but these latter are very easy of detection. The adulteration may consist of the entire substitution of margarine (oleomargarine) for the butter, in which case no difficulty is experienced in detection, or one or more of the above-mentioned foreign fats may be used, when small sophistications (under 10%) are often difficult to certify, especially if a judicious mixture has been used. Coconut oil probably seldom finds its way into butter directly, but as a constituent of substitutes. It is therefore absolutely necessary not to rely on any one test, the use of two or three reliable methods, however, being usually quite sufficient to detect the most skilful adulteration.

During the last few years, many methods have arisen for the purpose of detecting one or other form of adulteration in butter. As, however, many of these either fail to effect the required result, or are no advance on existing methods, only such are here given as are easy of application, of real utility, and which, with one exception, are used fairly generally. In all forms of butter fat analysis, reference to limits for true butter fat is an absolute necessity; a selection of the results obtained by various observers with each method is therefore given:

The methods here described are those which directly or indirectly obtain values for: (1) The refractive index of the fat; (2) the content of volable fatty acids soluble and insoluble in water; (3) the sp. gr. of the fat; (4) the mean molecular weight of the total fatty acids; (5) the mean molecular weight of the soluble and insoluble fatty acids.

1. **The Refractive Index of the Fat.**—This test is of considerable value for quickly detecting very flagrant adulteration; it breaks down in however the case of the more skilful forms of scientifically made mixtures. This will be understood when one considers that coconut and palm-kernel oils give a lower figure than butter fat, while beef fat, lard, and other adulterants give higher figures. It is obvious, therefore, that mixtures can be made to give the same reading as genuine butter fat. Notwithstanding this, the test is so quickly and easily performed, and so often affords immediate indication as to the direction of the adulteration, that it should not be neglected.

Several different forms of instrument are made for measuring the refractive index of fats.

The Zeiss *Butyro-refractometer* is by far the most convenient, requiring only about 5 drops of the fat; and reading with extreme delicacy. The scale is an arbitrary one, and may be converted to rerefractive index (N_D) if required. It should be noted that free fatty acids tend to reduce the reading, but the amount usually contained in butter fat is too small to produce any effect. Much confusion has arisen owing to there not being any fixed temperature at which to make the observation, and various workers have unfortunately chosen different temperatures. The most used temperature is 40°, and it is hoped that this will become universal. Readings taken at other temperatures may be converted fairly well by subtracting or adding 0.55 of a scale division for every degree rise or fall in temperature—the refraction being reduced as the temperature rises. In order that the reading may be taken at any temperature and quickly converted to the equivalent at the standard temperature, Leach and Lythgoe have devised a special slide rule to perform the calculation, and also to convert the Zeiss scale to N_D or *vice versa* if required. They take account of the fact that the correction is not the same for all fats. Richmond (*Analyst*, 1907, **32**, 44) criticises this rule adversely and points out sources of error. To avoid chance of error it is therefore better to take the reading at the temperature required, in which case the Zeiss water-heating apparatus should be used, by the use of which the prisms of the instrument may be brought to the required temperature in a few minutes, and maintained within a few tenths of a degree for a considerable time. Richmond (*ibid.*) gives the following method for the preparation of a correction chart:

"In the centre of a sheet of squared paper, at least 20 units by 12, lay out vertically the 35° line, dividing it into 100 parts. At the 109 line draw a line perpendicular to this on both sides and lay out temperatures 1°=0.7 unit; at the 24 line draw a similar line, laying out temperatures 1°=0.5 unit. Join the corresponding temperatures extending them to zero. These will be the temperature lines. On the 109 line find a point 8.5 units to the right; join this and 100 on the 35° line, extending it across the sheet; draw through each 5 on the 35 line lines of refraction parallel to this. To correct readings, find corresponding temperature and refraction lines. The correction is the number of units between lines corresponding to the temperature read and the temperature to which it is to be corrected, measured horizontally."

The following figures have been recorded:

Norwegian (Rifle), 38.7 (December) to 43.7 (June) at 45°; mean 39.5 to 41.95.

Russian (Lewin), 38.4 to 42.0 at 45°.

British (Thorpe) 371 samples from various farms and colleges. 37.3 to 43.0 at 45°.

Dutch (Bemelmanns), stall-fed cows 41.9 (November) to 43.2 (September), and for cows kept in the open field 43.3 to 47.6.

Dutch (Fritzsche), 42.0 to 45.4 at 40°.

Ludwig, for 110 samples of pure butter (1906) 40.0 to 43.6 at 40°.

Observation of the refractive index of the fatty acids themselves has been suggested. Reference should be made to Ludwig (*Zeit. Unters. Nahr.-Genussm*, 1907, **14**, 208; Sprinkmeyer and Fürstenberg (*ibid.*, 213); Sudendorf (*ibid.*, 217), and Dons (1906, **13**, 257).

2. **The Content of Volatile Fatty Acids, Soluble and Insoluble, in Water.**—(The words "soluble" and "insoluble" are relative. Soluble or insoluble in the quantity of water employed is meant.) Butter itself is distinguished by the large percentage of volatile water-soluble acids which it contains as compared with practically every other fat. The volatile water-soluble acids of butter are almost entirely butyric acid and caproic acid. The volatile water-insoluble acids are very small in amount and consist practically of caprylic acid, with traces of capric and lauric acids. Lard and oleo-products contain practically no volatile water-soluble acids, while in coconut oil and palm-kernel oil the volatile acids, though higher than in most fats other than butter fat, consist for the greater part of water-insoluble acids. These facts enable the following general deductions to be made:

1. Lard and oleo-products will reduce the percentage of volatile water-soluble acids.

2. Coconut oil will increase the percentage of volatile water-insoluble acids.

To ascertain the actual percentages of these acids is a difficult process, but the Reichert-Meissl-Polenske method allows of the estimation of such a quantity of these acids as shall give sufficient information. This process, which is described below, is a standard method. The result of a large amount of criticism is to show that the process must be carried out under standard conditions, and with the greatest attention to details, if comparative results are to be obtained by different observers. The details of procedure here given are of a standard nature and include Polenske's original dimensions for the apparatus.

A short table of limits is appended, but to avoid complication, no other figures are given here, as the Polenske figure depends on the type of apparatus, etc., used. As, however, the Reichert-Meissl figure is in itself a standard value in butter analysis, a large number of references to this figure are given. It must, however, be borne in mind that this figure also depends slightly on the form of apparatus, etc.

It is necessary to draw attention to the fact that the Reichert-Meissl figure is not lowered proportionately to the amount of added lard or margarine, and also that the addition of these produces a slight, but distinct increase in the Polenske figure in many cases, which might be taken as indicating coconut oil.

Many methods for the detection of coconut oil have been published during the last few years. As, however, none is any advance on the standard process here described, reference only to some of the papers is here given.

Hanus, *Zeit. Unters. Nahr.- Genussm.*, 1907, **13**, 18–24.

Robin, *Compt. rend.*, 1906, **143**, 512–514.

Dons, *Zeit. Nahr.-Genussm.*, 1907, **14**, 333–342.

Wijsman and Reijst, *Zeit. Nahr.- Genussm.*, 1906, **11**, 267–271.

The following table showing the Reichert-Meissl figures for Danish State Control butter for one year is exceedingly interesting. The rise and fall in the minimum figure is clearly marked, and the period of the year when low figures may also be expected.

R. M. No.	1906		1907									
	Nov.	Dec.	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.
30 and above	279	202	**468**	**636**	**1005**	**1063**	**831**	566	303	57	33	135
29–30	**456**	**474**	421	415	445	561	651	**696**	**699**	293	180	382
28–29	385	405	365	334	256	220	268	381	686	**593**	394	**393**
27–28	203	309	295	254	124	89	93	148	251	499	**457**	278
26–27	155	176	227	107	38	37	24	62	115	256	377	264
25–26	147	94	81	37	12	16	9	15	27	103	219	273
24–25	129	30	32	3	1	1	2	2	4	36	54	213
under 24 ...	98	13	11	0	0	0	0	0	1	9	18	99

For low Danish R. M. values see Swaving (*Zeit. Unters. Nahr.-Genussm.*, 1906, **11**, 505).

British butters (1901) (Thorpe) from a large number of farms and agricultural colleges. The table does not include Irish butters.

	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	April
Min.	26.5	26.0	22.5	23.4	22.4	22.3[1]	23.3	23.9	25.6	22.0	27.1	25.3
Max.	32.8	32.8	31.4	30.5	29.5	29.6	32.9	30.4	31.0	31.6	34.3	33.1

Norwegian butters (Rifle) 1898–1901.
Min., 21.1 June.
Max., 34.8 November.
Means, 28.5 (July) – 31.0 (Jan. and Feb.).

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[1] One farm gave 19.4.

German butters (Ludwig), 26.0–32.6 for 110 samples, 1906.

Dutch butters (Bemelmanns), 1905.

Stall-fed, 29.6 (Sept.) – 33.4 (March).
In open fields, 20.11 (Oct.) – 32.6 (March).

Note the low figure for the exposed cattle.

Australian and New Zealand (Theodor), 1903–04.

26.5 – 30.4. These butters are usually distinguished by high values.

Canadian (Theodor), 27.7 – 30.7.

The Reichert-Meissl figure is undoubtedly depressed in butter derived from cows that have been poorly fed and badly housed, especially in low temperatures. It is undoubtedly these causes which led to the low figures so common in Siberian butter, and which brought them under grave suspicion. The figure also shows a regular fall during the lactation period in individual cows, so that, when calving takes place almost entirely at one period, as for instance in Ireland, periods of low Reichert-Meissl values will be found. To obviate this, calving should be spread over the whole year. This is well seen in the following table (Handby Ball, *Analyst*, 1907, **32**, 202).

Dairy	Reichert-Meissl value	Polenske's new butter value	Zeiss butyro-refractometer 45°	Saponification value
Limerick	22.7	1.5	42.1	222.6
Bruree	21.5	1.5	42.2	221.5
Mallow	23.3	1.55	41.4	224.8
Clonmel	23.5	1.5	41.8	224.8
Tipperary	22.1	1.5	42.0	221.5

3. **Specific Gravity of Butter Fat.**—This was suggested by James Bell, who showed that melted butter fat is of sensibly higher sp. gr. than lard or margarine. Bell took the sp. gr. of the fat at 100° F. (37. 8°) by means of a sp. gr. bottle furnished with a thermometer, and his figures express the sp. gr. at 100° F., as compared with that of water at the same temperature. Some chemists take the sp. gr. at 100° and thereby greatly diminish the sensitiveness of the test, in that the difference between butter fat and most fats likely to be used as adulterants is not so great at the high temperature, owing to the greater coefficient of expansion of butter fat.

Skalweit (*J. Soc. Chem. Ind.*, 1894, **13**, 54) finds that the differences between butter fat and the fats likely to be used as adulterants are greatest at 35°, and this he shows in the following table:

Temperature	Lard	Margarine	"Butterine"	Butter fat
35	0.9019	0.9017	0.9019	0.9121
50	0.8923	0.8921	0.8923	0.9017
60	0.8859	0.8857	0.8858	0.8948
70	0.8795	0.8793	0.8793	0.8879
80	0.8731	0.8729	0.8728	0.8810
90	0.8668	0.8665	0.8663	0.8741
100	0.8605	0.8601	0.8598	0.8672

Bell gave 0.911–0.913 (113 samples) at $\frac{37.8°}{37.8°}$ as limits. They are, however, too narrow.

Thorpe for 361 samples of British made butters gave 0.90935–0.9135.

Lewin for Russian butters 0.911–0.91238, and for Siberian butters 0.91058–0.91204.

4. **The Mean Molecular Weight of the Total Fatty Acids.**—On account of the large percentage of esters of the lower fatty acids in butter fat, the mean molecular weight of the total acids will be lower than that of most fats, with the exception of coconut and palm-kernel oils. It therefore constitutes a valuable figure in the examination of butter fat. In practice it is usual not to actually determine the mean molecular weight, but the potassium hydroxide necessary to saponify 1 gm. of the fat. This value is called the Köttstorfer or Saponification Value. If the weight of fatty acids used is known, the mean molecular weight is easily obtained.

Lard and oleo-products and most other fats have a lower saponification value than butter fat, while coconut and palm-kernel oils have a higher value. It is therefore possible to adjust the admixture of these in butter in such a way that the saponification value is practically unaltered.

Köttstorfer gave 221.5 to 233.0 as limits for genuine butter.

Fritzsche for Danish butters 221.1 to 231.9, but for one department 217.7 to 218.9.

Bemelmanns for Dutch butters 226.5 to 235.1 (lowest in June and highest in March) for stall-fed cattle; and 213.0 to 232.9 (lowest in October and highest in March) for cattle kept in the open field.

Avé Lallemant for German butters, 220.3 to 241.1 (mean 227.4).

Thorpe for 347 samples of British butters, 215.8 to 239.8.

Arnold gives for margarine, 195.5 to 197.1; for oleomargarine, 196.4 to 198.0; for lard, 195.3 to 199.7; for coconut oil the value is 255 to 259; for palm-kernel oil the value is 243 to 250.

5. **Mean Molecular Weights of Soluble and Insoluble Fatty Acids and the Relation Between these Values.**—The data derived from methods involving directly or indirectly these estimations are of more value than any for the detection of adulteration. At the same time the available methods are long and laborious. The mean molecular weight of the insoluble fatty acids can be ascertained by the method of Hehner and Angell, *i. e.*, saponification of the fat, liberation of the fatty acids and the washing out of the soluble acids with large quantities of water, drying, weighing, and saponifying the insoluble acids. According to Juckenack and Pasternack (*Zeit. Unters. Nahr.-Genussm.*, 1904, **7**, 193), the mean molecular weights of both classes of fatty acids may be determined by steam distillation of the mixed fatty acids after acidification of the soaps. The acids being thus separated, their weights and saponification values are found and so the mean molecular weights. The following are limits obtained in this way by the latter authors:

Mean mol. wt. of water-soluble acids in pure butter, 95.0 to 99.0.

Mean mol. wt. of non-volatile acids in pure butter, 259.5 to 261.0.

Mean mol. wt. of water-soluble acids in coconut oil, 130.0 to 145.0.

Mean mol. wt. of non-volatile acids in coconut oil, 208.5 to 210.5.

Mean mol. wt. of non-volatile acids in lard, 271.5 to 273.5.

Olig and Tillmans (*Zeit. Unters. Nahr.-Genussm*, 1905, **10**, 728) give, however, for Danish butters (autumn) much higher values, viz., 255.4 to 271.6 for the non-volatile acids. Siegfeld (*Milch Zentralblatt*, 1905, **1**, 155) confirms these figures for autumn and winter Danish butters:

Mean mol. wt. of volatile acids, 97.2 to 104.4.

Mean mol. wt. of non-volatile acids, 255.0 to 269.1.

Arnold gives the following figures for lard compounds:

Mean mol. wt. of non-volatile acids, margarine, 272.6 to 275.0.

Mean mol. wt. of non-volatile acids, oleomargarine, 271.6 to 272.8.

Mean mol. wt. of non-volatile acids, lard, 272.4 to 275.8.

The writers using Juckenack and Pasternack's method have obtained rather variable results. The difficulty appears to consist in the fact that a variable quantity of the non-volatile acids is carried over mechanically during steam distillation, and no sharp dividing line is possible.

The following table showing the relation of soluble acids (calculated as butyric acid) to insoluble acids for a number of British butters is taken from values published by Thorpe.

	Minimum		Maximum	
	Soluble	Insoluble	Soluble	Insoluble
May	5.13	88.11	6.27	87.00
June	4.92	89.32	6.79	86.91
July	4.21	89.45	5.62	88.54
Aug.	4.31	89.76	5.73	87.99
Sept.	4.15	90.01	5.90	88.42
Oct.	3.77	90.73	5.61	88.49
Nov.	4.15	89.91	6.48	.....
Dec.	4.09	90.44	6.73	.....
Jan.	4.54	89.39	6.03	87.20
Feb.	4.09	89.71	6.04	87.60
March	5.00	88.73	6.67	87.36
April	4.86	89.00	6.44	.....

The method of Avé Lallemant (*Zeit. Unters. Nahr.-Genussm.*, 1907, **14**, 317) is directed to a very similar end, but in this case the barium saponification numbers of the acids forming water soluble and insoluble barium salts are determined. The method, though very recent, has been criticised most favorably by Fritzsche (*Zeit. Unters. Nahr.-Genussm.*, 1907, **14**, 329) and has, in the writers' hands, given such excellent results that it is here detailed in full as giving the most useful information. It is simple and easy of manipulation, and has the exceptional advantage that while giving evidence of the presence of either coconut oil or lard compounds, the effect of the presence of these together is additive and not mutually destructive as in many other forms of investigation. The actual mean molecular weights are easily determined by the use of the following formulæ:

B = Insoluble Baryta value (see below).
C = Soluble Baryta value (see below).
K = Saponification value.
U = Unsaponifiable matter.
M_0 = Mean mol. wt. of fatty acids forming insoluble barium salts.
M_1 = Mean mol. wt. of fatty acids forming soluble barium salts.

$$\left.\begin{array}{l} S \\ S_0 \\ S_1 \end{array}\right\} \text{ weight of } \left\{\begin{array}{l} \text{total fatty acids.} \\ \text{acids forming insoluble barium salts.} \\ \text{acids forming soluble barium salts.} \end{array}\right.$$

$$S_0 = \frac{M_0 \times B}{76.7} \div 1000.$$

$$S = 1 - (K \times 0.0002258 + U).$$

$$S_1 = S - S_0.$$

$$M_1 = \frac{S_1 \times 76.7}{C} \times 1000.$$

S_0 is directly estimated by drying and weighing the insoluble barium soaps and igniting.

As values for M_1 Avé Lallemant gives:

For butter fat,	110.3.
For lard,	281.1
For coconut oil,	145.8

The following figures are given by him:

Fat		R. M. fig.	a	b	c	b—(200+c)
Butter German	Maximum[1]	32.3	329.6	254.8	76.7	−23.8
	Minimum[1]	24.6	300.9	247.4	50.8	− 0.7
	Mean	28.7	310.7	250.7	60.3	− 9.6
Butter		29.9	313.0	253.0	60.0	− 7.0
Butter + 10% lard		26.3	306.7	254.6	52.1	+ 2.5
Butter		27.5	308.0	249.0	59.0	−10.0
Butter + 10% coconut oil		28.8	318.2	259.2	59.0	+ 0.2
Butter + 10% lard		26.0	311.7	258.2	53.5	+ 4.7

He states that butter has always a negative value for b−(200+c), while for a number of other fats it is always positive and not less than +39.0.

The writers are of the opinion that this formula must not be adhered to too strictly, as in certain cases with mixtures of butter fat and coconut oil negative values are obtained for b—(200+c), but in such mixtures they have always found the value for b to exceed 260.00, while in cases of butter fat which give only a very small negative value for b—(200+c) the value for c is always well below 260.00.

It must be borne carefully in mind that the values obtained in the methods given above have a distinct connection one with another. This is perhaps best illustrated by a study of the following table due to Thorpe.

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[1] The figures for a, b and c do not correspond, as they do not belong to the same sample.

357 samples of butter fat by Thorpe (*J. Chem. Soc.*, 1904., **73**, 254).

No. of samples	Reichert-Wollny number.	Sp. gr. 37.8°/37.8°	Saponification value[1]	Zeiss butyro-refractometer number at 40°	Soluble[2] acids % on fat	Insoluble acids % on fat	Mean molecular weight of insoluble acids
7	22.5	0.9101	219.65	42.0	4.3	90.1	266.9
17	23.5	0.9104	221.39	41.5	4.5	89.7	265.5
15	24.5	0.9108	223.24	41.5	4.7	89.4	265.0
27	25.5	0.9110	223.41	41.3	4.8	89.3	264.2
37	26.5	0.9113	225.39	41.0	4.9	88.9	261.9
51	27.5	0.9114	226.75	40.6	5.2	88.7	261.7
78	28.8	0.9118	228.32	40.1	5.4	88.4	260.9
56	29.5	0.9120	229.91	40.1	5.6	88.3	259.6
41	30.5	0.9123	231.43	39.9	5.8	87.9	260.1
18	31.3	0.9125	232.30	39.7	5.7	87.9	258.0
10	32.6	0.9130	232.58	39.4	6.0	87.7	257.8
357							

The following table gives a few results obtained by the writers using the above methods:

	Val.	Iod. No.	R. M. Val.	Pol. Val.	Sap. Val.	Total Ba (a)	Insol. Ba (b)	Sol. Ba (c)	b—(200+c)
Butter A........	28.8	33.9	28.7	3.2	228.4	312.2	255.4	56.8	−1.4
Butter A + 10% coconut oil	25.2	31.4	26.6	4.1	231.1	315.9	262.8	53.1	+9.7
Butter B........	30.3	36.5	28.1	2.5	227.8	311.4	254.8	56.6	−1.8
Butter B + 10% coconut oil	26.4	33.7	25.8	3.9	230.3	314.8	260.5	54.3	+6.2
Butter C........	27.0	35.7	30.5	3.5	227.0	310.3	255.1	55.2	−0.1
Butter C + 10% coconut oil	24.0	32.8	28.0	4.3	230.5	315.1	263.6	51.5	+12.1
Butter D........	30.2	38.7	30.8	2.9	224.8	307.3	252.8	54.5	−1.7
Butter D + 10% lard	35.2	40.6	27.7	2.4	221.8	303.2	254.6	48.6	+6.6

Estimations.

Butter fat is conveniently prepared from butter. The required quantity is melted in a beaker by standing in water at 50° to 60°.

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[1] Calculated by Lewkowitsch from the saponification-equivalents given by Thorpe.
[2] Calculated as butyric acid.

As soon as the water and the bulk of the curd have settled, the fat is poured on to a dry, warm, thick, plaited filter, keeping the filter warm during filtration. The fat so obtained should be clear and bright; if not so, it should be warmed and refiltered. The fat must at no time be heated above 60°.

The following method due to Stokes is excellent, especially when only a small quantity of the fat is wanted quickly. A strong tube about 6 in. long and 0.75 in diameter, tapered at one end, is used. Both ends are open, and can be closed with corks. The tube is warmed and pushed through the butter till the tube is full. The corks are inserted and the tube placed in water at about 55° to 60° until the contents are liquid, rotated while warm and then a good plug of dry absorbent cotton wool is pushed down through the fat by means of a perforated metal plunger fitting the tube. The fat passing the cotton is obtained clear and bright and ready for use. By having the small end of the tube graduated, a rough idea of the water content is also obtained.

1. **Construction and Mode of Action of Wollny's Butter Refractometer; Zeiss' Butyro-refractometer.**—The butter refractometer consists of a heatable Abbé double prism and a permanently attached telescope, the objective of which is adjustable in a slide by means of a micrometer screw. A scale, graduated from 5 to 105, is placed in the focal plane of the telescope objective; the upper lens of the ocular is adjustable in order to be able to focus the lines and figures of the scale clearly.

Clear daylight is projected into the double prism by the mirror (J) and penetrates through the stratum of fluid between the prisms. The naturally coloured border-line of total reflection, produced by this passage of rays in the focal plane of the telescope, hence also in the plane of the scale, is achromatised in the case of pure butter by virtue of the special construction of the glass prism turned toward the telescope. Thus a sharp colourless border-line, which intersects the scale vertically, is seen in the ocular between a light and a dark section of the field of view. The accuracy of the measurement to be made then depends on the exact determination of the point in the scale through which the border-line passes. With the aid of a detailed table supplied with each instrument, the divisions of the scale can be converted into refractive indices.

Arrangement of the Refractometer and of the Heating Appliance.—The apparatus is withdrawn from its case by taking hold of the base plate or the telescope carrier—never the telescope itself—and placed in a convenient position for looking into the telescope. The illumination may be supplied either by the daylight coming in through a window or by the light of a lamp.

The refractometer can be used in conjunction with any kind of heating appliance which affords a current of water of constant temperature and uniform speed. Connection with the refractometer should always be established so that the water enters at D and flows off at E.

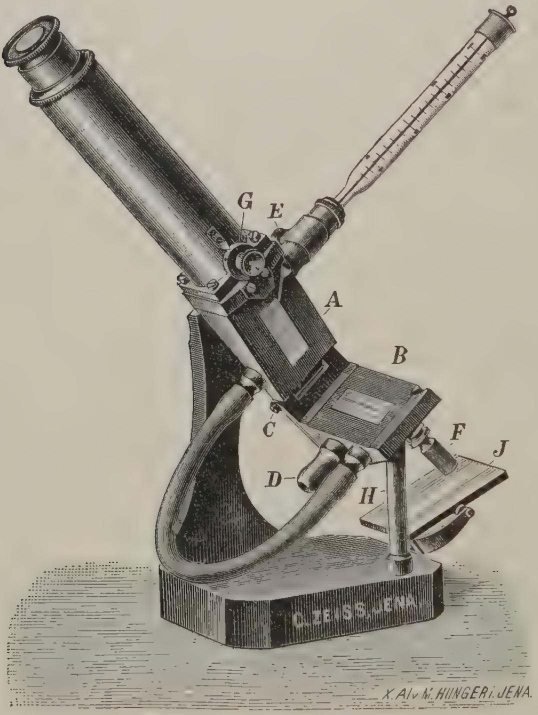

FIG. 9.

Application of the Sample of Butter to the Prisms.—The prism casing is opened out by revolving the screw-head, F, clockwise, giving it a half-turn until checked, when one half (B) of the prism casing can simply be hinged down. The post H keeps B in the position shown in the figure. The surfaces of the prisms and of the metal parts must now be cleaned with scrupulous care, soft clean linen and a little alcohol or ether being best for the purpose.

A small quantity of the sample of butter to be tested is then melted down in a little spoon and poured upon a small filter of blotting-paper, held in one hand. The first two or three drops of clear butter fat percolating the filter are applied to the surface of the folding prism, in doing which it is expedient to tilt up the apparatus with the left hand, so as to bring the surface in question to an approximately horizontal position. The filtering of the sample of butter is not absolutely necessary. The quantity required for the test may be taken up by means of a glass rod, but the precaution of carefully rounding the ends of the rod and of avoiding impurities floating on the surface of the melted butter should not be disregarded.

The observer now presses the component B against A and turns the screw-head, F, in the reverse direction to contact with another stop, whereby B is secured against dropping back and close adhesion of the two prism surfaces is effected as well. The apparatus is at the same time replaced on its base plate.

The mirror, J, should be arranged in such a position that the border line appears distinctly, which may necessitate slight shifting or turning of the entire apparatus. The draw at the ocular should also be adjusted so that the scale can be seen distinctly.

The first thing necessary is to ascertain that the entire space between the prism surfaces is uniformly packed with butter fat. For that purpose the small image of the prism surface, situated about 1 cm. in front of the ocular, is scanned with a magnifier (or with the naked eye), held at the requisite distance from the ocular. In this way minute air bubbles within the stratum of fat, which would prejudice the sharpness of the border-line, will be readily detected.

If a current of water of constant temperature has previously circulated for a time through the prism body, the border-line will quickly, generally in about a minute, assume a fixed position and attain the maximum of sharpness. Both being obtained, the appearance of the border-line (whether colourless or, if coloured, the tint) also the position of the border-line relatively to the scale are noted, and at the same time the temperature registered by the thermometer read off.

Integral divisions of the scale are read off immediately in the field of view, tenths of a division being determined by the aid of the micrometer screw (G in Fig. 9) in the following manner. The border-line is adjusted by means of the screw upon a division of the scale, when the micrometer drum will indicate the number of tenths to be added to the number of integral parts of the scale appertaining to the particular division. If a number of tests are being made in immediate succession, a little practice, with the help of an assistant to attend to the melting and hand the small samples of butter, will make it easy to carry out the refractometrical test of from 25 to 30 samples of butter in the space of 1 hour.

Wollny has devised a special thermometer which indicates the highest admissible values for genuine butters at temperatures varying from 30° to 40°. A standard fluid is provided for the purpose of testing the adjustment of the ocular scale and directions are given for resetting the scale when necessary.

The use of sodium-light illumination greatly sharpens the border-line.

2. *The Reichert-Meissl-Polenske Method.*—In this process the saponification is conducted according to the method devised by Leffmann and Beam. 5 grm. of the fat and 20 grm. of glycerol are weighed into a 300 c.c. flask and 2 c.c. of 50% sodium hydroxide solution added (made by dissolving good sodium hydroxide in an equal weight of water and allowing to stand till clear). The flask is heated over a flame with constant shaking, till it clears suddenly. Cool the soap and add 100 c.c. of recently well-boiled distilled water, till solution of the soap is effected. 0.1 grm. of powdered pumice sifted through muslin (the grade and quantity are important) is added and then 40 c.c. of sulphuric acid solution. (20 c.c. of sulphuric acid diluted to 1,000 c.c., and the solution adjusted so that 35 c.c. neutralise 2 c.c. of the sodium hydroxide solution.) The flask is at once connected to the condenser, and heated with a small flame till the insoluble acids are completely melted; the flame is then increased and 110 c.c. distilled in 19 to 21 minutes. Condenser water should be from 18° to 20°, and dimensions of apparatus exactly as shown in Fig. 10. When 110 c.c. have distilled, the flame is removed and a 25 c.c. cylinder placed under the condenser to catch any drops. After mixing the contents of the 110 c.c. flask, they are filtered and 100 c.c. titrated with N/10 alkali, using 0.5 c.c. of a 1% alcoholic solution of phenolphthaleïn as indicator. This number of c.c. increased by 1/10, after subtrac-

tion of the blank (which must be determined in an exactly similar way by using all the reagents except the fat) is the Reichert-Meissl value. The condenser, cylinder, and 110 c.c. receiver are washed with 18 c.c. of cold water, which are then poured over the filter used to filter the distillate. The condenser is washed out with four successive portions of 10 c.c. of neutral alcohol, which are received in the cylinder and poured successively into the 110 c.c. flask and over the filter, the mixed alcohol solutions being then titrated with N/10 barium hydroxide, using phenolphthaleïn as indicator. A blank value is obtained in a similar way. The number of c.c. of N/10 barium hydroxide used less the number used for the blank is the Polenske figure or New Butter Value.

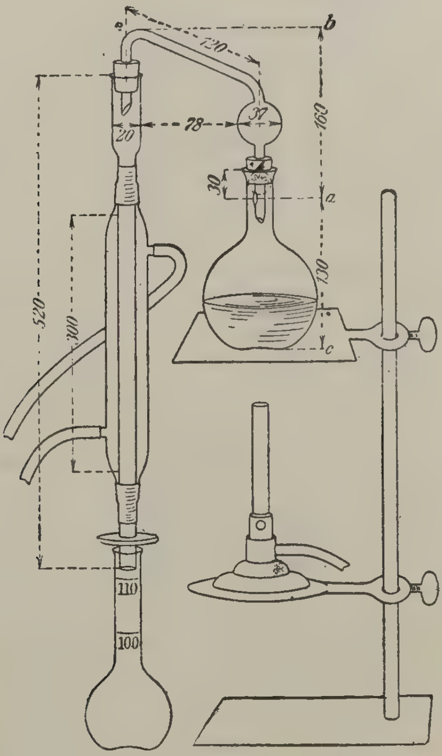

FIG. 10.

Rather varying results have been obtained by various observers, but the following table will be found a very fair guide:

Reichert-Meissl values	New Butter values
32	3.5
31	3.2
30	3.0
29	2.9
28	2.7
27	2.4
26	2.0
25	1.8
24	1.7
23	1.6

A "New Butter Value" exceeding by 0.5 c.c. the figure corresponding with the Reichert-Meissl value found, indicates the presence of coconut or palm-kernel oil or coconut "stearine."

If an approximate idea of the amount of coconut oil present is desired, Polenske's original table (*Arbeit aus dem Kaiserl. Gesund.*, 1904, **20**, 543) should be consulted (reproduced in Lewkowitsch: Oils, Fats and Waxes, Vol. ii, p. 702, 4th Ed.).

It has been stated that the presence of oily drops in the first distillate (after cooling at 10°) is distinctive of coconut oil, but this is undoubtedly fallacious. Many chemists also employ only 90 c.c. of water for solution of the soaps and 50 c.c. of sulphuric acid solution (25 c.c. sulphuric acid to 1,000 c.c. with water).

For the Reichert-Wollny method see Margarine.

3. *Specific Gravity of the Fat.*—This is best determined in a 25-grm. bottle. The dry melted fat is run into the bottle a few degrees below the temperature at which the gravity is to be observed, great care being taken that no air bubbles are introduced at the same time. The stopper is screwed gently home and the bottle immediately immersed in water of the desired temperature for 45 minutes. The test is then finished in the usual manner. For convenience, especially if many determinations are made, a bath regulated to the temperature by means of a thermostat may be used.

4. *Saponification Value* (Köttstorfer Value).—The saponification value is defined as "the number of mg. of potassium hydroxide, which is necessary to completely saponify 1 grm. of fat."

(Saponification equivalent is the number of grm. of butter fat saponified by 56.1 (*i. e.*, one equivalent) of potassium hydroxide. It is obvious that this is merely another mode of expressing the same result, and the one figure can easily be calculated from the other. Köttstorfer's original mode of expression is now more generally used.)

Solutions required: 1. N/2 hydrochloric acid accurately prepared. 2. Alcoholic potassium hydroxide approximately N/2 strength. 3. 1% alcoholic solution of phenolphthaleïn.

The potassium hydroxide solution is prepared by dissolving 17 to 20 grm. of stick potassium hydroxide (purified by alcohol) in the smallest possible quantity of water, and then making up to 500 c.c. with alcohol of not less than 94% (by weight). The solution is allowed to stand over-night, and the clear liquid syphoned off for use. If the alcohol is pure, the solution will be colourless, or nearly so (it is advisable to test the alcohol before making up the solution and rejecting any which gives more than a very pale colour when boiled with a strong solution of sodium hydroxide).

The test is carried out as follows:

About 2 grm. of the clear melted and filtered fat are weighed into a 200 c.c. Jena flask, and an accurately measured quantity of the alcoholic potassium hydroxide solution run in from a 25 c.c. pipette. A like quantity of the same solution is run from the same pipette in exactly the same way into a clean 200 c.c. flask. The flasks are connected to reflux condensers and heated in a water-bath so that the alcohol gently boils; this is continued for 30 minutes. The flask containing the butter fat should be shaken occasionally, particularly at the commencement. The flasks are removed from the bath, 20 drops of phenolphthaleïn solution added to each, and the contents titrated while hot with the N/2 acid.

If F = grm. of fat taken.
X = c.c. of acid required in the control experiment.
Y = c.c. of acid required to neutralise the excess of alkali in the test.

Then sap. value $(S) = \frac{(X-Y) \times 0.02805 \times 1000}{F}$,

and saponification equivalent $= \frac{56100}{S}$.

5. *The Barium Method of Avé-Lallemant.*—1.9 to 2.0 grm. of the filtered butter fat are saponified with 25 c.c. of approx. N/2 alcoholic sodium hydroxide (carefully standardised), boiling for 30 minutes; while still warm, titrate with N/2 hydrochloric acid to phenolphthaleïn. The alcohol is removed as completely as possible by boiling and blowing air into the flask. The soap is dissolved in 150 to 180 c.c. of hot recently boiled distilled water, in a 250 c.c. flask. Stand on the water-

bath 5 minutes, and add 50 c.c. of approximately N/5 barium chloride solution (25 grm. crystallised barium chloride in 1,000 c.c.). Allow to remain 15 minutes on the water-bath to cause the insoluble barium salts to coalesce. Cool, fill to the mark with water and filter off 200 c.c. into a beaker, heat this to nearly boiling on a sand-bath, add 1 c.c. hydrochloric acid and 10 c.c. of approx. N/1 sulphuric acid. Filter the barium sulphate on a gooch crucible, wash till free from chlorides, and finally with two quantities of 10 c.c. of warm alcohol. Dry to constant weight. Increase the weight of barium sulphate found by 25%, and calculate to BaO ($BaSO_4 \times 0.6571$ = barium oxide). Subtract this last from the barium oxide value of the barium chloride solution (which must be standardised in an exactly similar way). This gives the barium oxide value of the acids forming insoluble barium salts. Calculate this to 1 grm. of fat = insol. barium oxide value (b). The saponification value is also calculated as barium oxide ($KHO \times 1.367$ = barium oxide) for 1 grm. of fat = total barium oxide value (a), then $a - b$ = sol. barium oxide value (C), and so find $b - (200 + C)$.

After much experience with this method, the writers advise the use of 5 grm. of fat for the test. After saponification and removal of the alcohol, the soaps are made up to 250 c.c. with water at 38°, and 100 c.c. pipetted off at that temperature for the estimation of the barium oxide, the test being finished as above. By this means a more accurate figure is obtained for "a."

Qualitative Tests.

The above quantitative examinations may be supplemented when desirable by one or more qualitative tests. These are useful more especially as confirmation of the presence or nature of some adulterant indicated by the quantitative figures. Some of them are sometimes used as "sorting" tests.

1. *Microscopical Appearance.*—When genuine butter is examined in a thin film, under a low power (×25 to 50 diam.) between crossed nicols, it appears as a homogeneous mass, but if it has been melted, bright specks or patches, or sometimes even crystals, giving a play of colours with a selenite plate, may be noticed. Margarine (oleomargarine) has a similar appearance to butter which has been melted and reset.

This test may be used for rough sorting out purposes, setting aside for further examination all samples showing crystalline structure. It is advisable to place a cardboard tube around the objective and enclosing the preparation, so as to exclude adventitious rays.

2. *The Foam Test.*—(*Farmers' Bulletin, U. S. Dept. Agric.*, No. 131.) This is a rough and ready method of distinguishing butter substitutes and renovated butter from genuine butter. In fact, it is especially valuable in the case of renovated butter, the chemical composition of which is the same as true butter.

A lump of about 5 grm. of butter is melted in a spoon over a very small bunsen flame; genuine butter boils quietly, producing considerable foam, while butter substitute and renovated butter crackle loudly and splutter, but do not produce any appreciable quantity of foam.

It will further be noticed that on melting genuine butter, the curd separates in a very finely divided state, while in the case of margarine and renovated butter the curd is lumpy.

A few trials of this test will enable the operator to see differences which are difficult to describe in words.

Wanklyn's Test.—The production of ethyl butyrate, when butter fat is heated with alcoholic solution of alkali, may be used as a sorting test for distinguishing "straight" oleos (that is butter-substitutes containing no appreciable amount of butter fat). The test is most satisfactorily applied by the method described in Leffmann and Beam's "*Select Method of Food Analysis*," 2d Ed., 236. A few grm. of the sample (which need not be filtered) is placed in a test-tube, about 10 c.c of strong solution of sodium hydroxide in alcohol added, the mixture heated until it foams actively, and then promptly poured into about 100 c.c. of cold water. The pineapple odour of ethyl butyrate is at once noticeable if appreciable amounts of butter are present. Care must be taken not to mistake the somewhat aromatic odour of the alcoholic solution for that of true ester. The nature of the reaction is not known.

3. *The Valenta Test.*—The glycerides of the saturated fatty acids present in butter have varying solubility in pure acetic acid. The temperature at which a solution of the fat in acetic acid begin to deposit solid glycerides varies with the constitution of the mixture. Butter itself shows a turbidity within reasonably close limits under strict conditions of experiment. The addition of the glycerides of the higher fatty acids, as by the use of lard and similar products, causes the turbidity temperature to rise, while the addition of the glycerides of the lower members of the series, such as is brought about by the use of coconut

and palm-kernel oils, will lower the temperature. The test, therefore, if carefully performed, is of real value, especially as confirmatory or diagnostic of adulteration by lard products.

Many methods of carrying out the test have been proposed, but the following is simple and easy and quite sufficient. A long thin test-tube, preferably of Jena glass, about 0.5 in. in diameter, and sufficiently long to take in the scale of a thermometer up to 60°, is marked accurately at 3 and 6 c.c. with lines all round the tube. A thermometer with very small bulb is fixed in the tube by means of a cork, so that the bulb is opposite the 3 c.c. line. The carefully dried butter fat (filter-paper pellets should be shaken up with it beforehand) is measured in at 27 to 29° till the bottom of the meniscus coincides with the 3 c.c. line. Absolute acetic acid (Kahlbaum's is to be preferred) is then run in until the 6 c.c. line is reached (the acid should be measured at a definite temperature, say 15 to 16°). The thermometer is inserted and the fat dissolved by shaking in water at about 50°. The tube is then withdrawn, and the contents allowed to cool in the air, shaking gently, and holding the tube in a good light. Immediately the faintest turbidity is noticed the temperature is read. The tube is then slightly warmed and a fresh reading obtained. The end point is quite sharp, and consecutive readings should scarcely differ.

It must be carefully borne in mind that every operator should obtain figures for himself for pure butters, as the least change, especially in the acid, produces a change in the results. Operating in the above manner, the writers have found butter to vary between 25° and 44.4°, mostly between 37° and 42°. The greatest variations were found in Danish State Control butters. 10% of lard produces a rise of about 7°.

4. *Halphen's test for cottonseed oil and cottonseed "stearine"* may be carried out as follows: 2 to 3 c.c. of the melted fat are dissolved in an equal volume of amyl alcohol in a test-tube, 2 to 3 c.c. of a 1% solution of sulphur in carbon disulphide added, and the tube is placed in a boiling water-bath for 20 minutes. In the presence of cottonseed oil, or cottonseed "stearine" a characteristic crimson colour is produced. This test is capable of detecting less than 5%. It is possible to treat cottonseed oil so as to evade this test, but this is not usually done. The test is applicable to the acids from cottonseed oil.

The test will detect 1% of cotton seed oil if the heating be done in closed test-tubes.

5. *Baudouin's Test for Sesame Oil.*—Take 10 c.c. of the melted fat in a test-tube, add 2 drops of a 2% alcoholic solution of furfural, and 10 c.c. of concentrated hydrochloric acid. Shake for a minute. In the presence of sesame oil the aqueous layer will be a crimson colour. The test is sensitive to 1%, but certain azo dyes interfere with the delicacy.

Sprinkmeyer (*Zeit. Unters. Nahr. u. Genussm.*, 1908, **15**, 20–21) states that rancid cottonseed oil prevents the red colouration unless 17% of sesame oil is present.

6. *Phytosterol and Phytosteryl Acetate Test for Vegetable Fats and Oils, Including Coconut Oil.*—Boil 50 grm. of the clear fat with 75 c.c. of 95% alcohol. Cool and pour off the alcohol and repeat the extraction with a further 75 c.c. The combined extracts, which will contain the bulk of the cholesterol and phytosterol, and some fat are transferred to a porcelain basin, and an excess of solid sodium hydroxide having been added, evaporated, stirring occasionally. After the bulk of the alcohol has gone, add more than sufficient sodium hydrogen carbonate to convert the sodium hydroxide to carbonate, then sand and carry to dryness. Grind up the dry residue in the dish and extract with light petroleum. The residue from the ether is treated with 5 c.c. of approx. N/2 alcoholic sodium hydroxide and again evaporated to dryness with sand. Re-extract with petroleum ether, evaporate, and take up with the smallest possible quantity of absolute alcohol. (If much coloured, boil first with a small quantity of 95% alcohol and a little finely divided animal charcoal, filter, and evaporate to dryness). Allow to crystallise and examine microscopically. The residue is converted into acetate and recrystallised in the usual manner.

Juckenack and Pasternack (*Zeit. Unters. Nahr. u. Genussm.*, 1904, **7**, 193–214) give from 113.2° to 114.6° (corr.) as the m. p. of the cholesteryl acetate of pure butter (after 5 crystallisations), and from 117.2° to 122.6° (corr.) for that obtained from butters adulterated with varying quantities of coconut oil.

It has been proved that animals fed on oil cakes sometimes produce a butter fat giving indications of the oil present in the cakes, notably by Halphen's test, but phytosterol has not been found in butter fat from animals so fed.

7. *Hinks' Test* (*Analyst*, 1907, **32**, 160).—This is a valuable qualitative test for coconut and palm-kernel oils. It is based on the fact that

the latter contain a fat which crystallises from alcohol in a characteristic form. To one who has once become familiar with the shape of the crystals, the test is valuable and reliable, but without this experience, and if not carried out exactly as recommended it may prove misleading. The writers have been able to detect 2.5% of coconut oil in this way.

The test is carried out as follows:

5 c.c. of the clear fat are dissolved in twice their volume of ether, in a wide test-tube, and packed in ice. After 30 minutes (much solid fat will have separated) the whole mass is thrown on a plaited filter. The filtrate is evaporated in a basin and heated on a boiling water-bath. The residual fat is poured into a test-tube, and 3 to 4 times its volume of alcohol (96 to 97% by volume) added. Boil, when solution will be effected. The tube is then kept in water at 5° for 15 minutes, and the alcoholic layer is then rapidly filtered into another tube, which is then kept at 0° for 2 or 3 hours.

After this time a portion is withdrawn by a glass tube, dropped on a slide, covered without pressure, and immediately examined at a magnification of 200 to 300 diameters. (The examination must be quickly carried out, as the crystals are soon redissolved as the liquid warms. In hot weather a cooled stage is necessary, conveniently made by placing a flat piece of ice contained in a petri dish under the slip.)

Butter crystallises in round granular masses, but if coconut or palm-kernel oil is present, numerous fine feathery crystals will be seen as well. Lard, however, produces crystals which are not unlike those from coconut and palm-kernel oils.

Butter.

The examination of butter itself, apart from the special examination of the butter fat, consists usually of the estimation of water, fat, curd, and salt. By "curd" is usually meant the solids-not-fat, without the mineral constituents, which are usually included under the general term "salt." For special purposes, the actual percentage of proteins is estimated and also the actual percentage of salt as sodium chloride. Besides these, an investigation into the nature of the colouring matter and preservative (if any) present, is often necessary.

Such an examination is of value for the purpose of ascertaining whether a butter is properly made, whether it has been properly worked so as not to include an excess of moisture, and also whether any addition of milk (whole or condensed), casein, dried milk, or of other similar substances has been made, such additions having been rather frequently made of late years. For an excellent paper on the "Physical Constitution of Butter" see Bean (*Rev. Gén. de Lait.*, 1904, **10**, 224).

Before passing to consider the various constituents, it may be well to briefly quote the regulations enforced in various countries (1906).

Canada.—Maximum limit for water 16%. No renovated or process butter to be made or imported.

New Zealand.—Butter to be made only from milk or cream and to contain only salt, and certain preservatives and colouring matters. Grading is by government officials and butter is officially marked.

Queensland.—Maximum limit for water 16%. Minimum limit for fat 80%.

No extraneous ingredients, except harmless colours or preservatives, such as boric acid and borax (not more than 0.5% as boric acid). Butter is officially marked.

Victoria.—Maximum limit for water 15%. Minimum limit for fat 80%.

Denmark.—Butter control official since May, 1904. The creameries form associations and must not be connected, directly or indirectly, with the manufacture of margarine or edible oils. The chemical analyses of every creamery are known and recorded.

Belgium.—Maximum limit for water 18%, unless declared. Butter is regarded as abnormal and prohibited for sale if, (1) The Reichert-Meissl figure is below 28, and if (2) in addition, the fat gives one of the following values:

(a) Refraction (Abbé-Zeiss) above 44 at 40°.
(b) Sp. gr. below 0.865 at 100°.
(c) Saponification value below 222.
(d) Hehner value above 88.5.

Germany.—(1902) Minimum limit for fat 80%. Maximum limit for water 18% (unsalted butter). Maximum limit for water 16% (salted butter).

Italy.—Minimum limit for fat 82%.

Butters with R.-M. value 26 or above are pure.

Butters with R.-M. value 20 to 26 are suspicious.

Butters with R.-M. value below 20 are adulterated.

Refraction (Zeiss) not to be above 48 at 35°.

Sp. gr. not to be below 0.865 at $\frac{100^\circ}{15^\circ}$.

No preservatives, except common salt and boron mixtures, which shall not be present in greater quantity than 0.3% reckoned as boric acid.

United States of America.—Minimum limit for fat 82.5%, and in renovated and process butter, not more than 16% of water.

Reichert-Meissl value not less than 24.

Sp. gr. at 40°/40° not less than 0.905, but there are different regulations in different States.

England.—Maximum limit for water 16% and in milk-blended butters 24%.

1. **Water.**—Apart from the examination of the fat, this estimation is the most important. The percentage of water in butter varies naturally for many reasons. The method of churning, and especially the temperature of churning, is a most important factor in determining the quantity of water left in the worked butter. Taking 60° F. as roughly the correct churning temperature, then temperatures decidedly above, or decidedly below this, will result in the inclusion of too much water. At elevated temperatures a very large quantity of water can be worked into and retained by the butter, as is found in the case of Irish "pickled" butters, and butters so made are often quite firm, and do not even appear moist. The addition of salt tends to produce a drier butter, though the appearance of a salt butter would lead to an opposite conclusion, seeing that moisture exudes from "salt butters" in small drops when cut. There is no difficulty, in properly managed churning operations, in keeping to a fairly constant water content, and for this reason, in most countries a maximum percentage for water is either legally or tacitly enforced.

It seems to be generally agreed that butters containing 13 to 14% of water have the best flavour.

Canadian Butters.—The Dept. of Agriculture gives 12.3% as the average of a large number. Theodor, in 1903–04, gives 9.2 to 15.5%.

New Zealand.—(1905) Average 10.59. Theodor gives 9.9 to 11.7 (1903–04).

Australian.—10.0 to 13.6% (Theodor).

Danish.—From 1897 to 1900, 95.2% of butter contained between 12.0 and 16.0% of water.

From 1897 to 1904, in butters supplied to Canada by Denmark, a steady increase from 13.79 to 14.25 was found by the Dept. of Agriculture, Ottawa.

Irish Firkin Butter.—Twooney (Report of Dept. Committee, 1906, England) gives the following percentages of butters containing more than 16% of water.

Season 1902–3	(53,166 samples)	7.49%.
Season 1903–4	(49,197 samples)	5.06%.
Season 1904–5	(40,464 samples)	7. 7%.
Season 1905–6	(35,359 samples)	3.87%.

2. **Curd.**—Under this term is usually included the total solids-not-fat, less the ash. It is rather a variable figure, and depends very much on the method of and care in making. The curd is likely to be much higher in the case of butters made from whole milk than from cream, but as the former is scarcely made to-day, certainly not for the market, it does not much concern the analyst. In properly made butters the curd varies from very small amounts to 2.5%. The higher limit is rare and probably 1.0 to 1.5% is most usual. As this estimation is chiefly of value for the detection of the addition of condensed milk, casein, etc., it is far preferable to actually determine the protein. When this estimation gives more than 1.0% of casein, it may be taken as almost certain that addition of milk products has been made. In such cases there is usually an excess of water, and if whole or dried milk has been worked in, an estimable amount of lactose will probably be found.

3. **Ash.**—This term usually includes salt and preservative, as well as mineral constituents of the original cream. It is sometimes necessary to actually estimate the sodium chloride present. In fresh butters only a trace of chlorides will be found, while in salt butters even 12% may occur, the quantity of salt present being almost entirely controlled by the taste of the consumer.

The careful estimation of the various constituents of curd and ash is only necessary when forms of adulteration are suspected which are not easily apparent. The question of preservatives and colouring matters is now practically determined by the law of the country concerned.

The following table gives a number of values for water, curd, salt, etc., for various butters:

Butter	Water		Casein $N_2 \times 6.39$	Sugar	Salt	Ash
German, 364 samples (Hesse)	Summer max.	12.80	0.60	0.52	1.32	0.12
	Summer min.	11.67	0.51	0.45	1.02	0.10
	Summer mean	12.31	0.57	0.50	1.17	0.11
	Winter max.	12.70	0.74	0.64	1.62	0.12
	Winter min.	12.29	0.66	0.55	1.34	0.09
	Winter mean	12.50	0.68	0.59	1.40	0.11

Vieth gives the following analyses:

Butter	Fat	Curd	Salt	Water
English	86.85	0.59	1.02	11.54
French	84.77	1.38	0.09	13.76
French (salted)	84.34	1.60	2.01	12.05
Kiel	85.24	1.17	1.35	12.24
Danish	83.41	1.30	1.87	13.42
Swedish	83.89	1.33	2.03	13.75

Estimations.—For exact analysis, care must be taken to get a representative sample. From a small sample a piece may be cut from opposite corners and from the middle. From a large bulk, a suitable piece is cut from within the bulk by means of a fine wire. In either case, the sample is then placed in a 4-ounce stoppered bottle, the fat melted by standing in water at about 50°, shaken to the consistency of cream, and weighed out while in this state.

1. **Water.**—2–3 grm. of the sample are weighed out into a large weighing bottle, 2 inches deep and 1.5 inches wide, and having parallel sides and dried in the water-bath at 100° (shaking every 10 minutes), to constant weight (2 to 3 hours). As soon as the curd has stuck to the bottom, the bottle should be tilted on its side, drying being much facilitated.

The following method, due to Patrick (*Jour. Amer. Chem. Soc.*, 1906, **27**, 1613) is exceedingly useful for control purposes or for sorting samples. About 10 grm. of butter are weighed into an aluminium beaker (a wide glass test-tube may be used), and the water gently boiled off over a naked flame, until the hissing sound which accompanies the evaporation of the water ceases. Care must be taken to avoid overheating and consequent discolouration of the butter. Foaming may be reduced by heating the upper part of the beaker or tube. Patrick gives −0.10 to +0.17 as the limits of deviation from results obtained by the official A. O. A. C. method.

2. **Fat.**—This is usually estimated by extracting the dried residue from the water determination with five successive quantities of ether, allowing as long as possible for the ether to act at the fourth extraction. The ether is poured off carefully each time, and no loss need occur. The residue is dried and weighed, the difference between the weights before and after extraction giving the fat.

For accurate estimations of the fat, the Gottlieb method is to be preferred. The method as given by Hesse (*Zeit. Unters. Nahr. u. Genussm.*, 1904, **8**, 673) is as follows: 1.5 to 2 grm. of the sample are weighed into a long graduated tube with 8 c.c. of warm water and the fat completely melted by placing the tube in hot water. Add 1 c.c. of 10% ammonia and 10 c.c. of strong alcohol, mixing well between and after each addition, and the mixture well cooled. 25 c.c. methylated ether are added; the liquids mixed by inversion; 25 c.c. petroleum ether (distilled below 60°) added, and again mixed three times by inversion. The mixture is allowed to separate; the ethers pipetted off; 50 c.c. of ether again added and pipetted off without shaking; then the mass is shaken out finally with 25 c.c. ether and 25 c.c. petroleum ether and pipetted off as before. The mixed ethereal solutions are evaporated and the fat weighed. The last addition of ethers may be omitted without serious error.

3. **Curd.**—This may be estimated in the residue from the fat estimation by breaking up carefully and extracting with water, the insoluble residue being finally washed on to a tared filter, which is then dried at 100° and weighed. The filter should then be incinerated and the ash deducted from the weight of curd. While this method is useful, when only an approximate idea of the curd be required, if a proper estimation of the protein is desired, especially when the milk-sugar is to be ascertained by difference, the nitrogen should be estimated by the Kjeldahl process (*q. v.*) using 6.38 as the factor.

In this estimation about 12 grm. of butter are weighed into the digestion flask, and rapidly dried by placing the flask in boiling water and exhausting the interior. About 20 c.c. of ether are added and the curd allowed to settle. The ether is poured off (if turbid, through a small filter), the curd washed once again with a little ether, and after evaporating all traces of ether from the flask, the sulphuric acid digestion proceeded with. If a filter has been used, this is dropped in before digestion. If the fat is not thus removed, serious charring will take place.

4. **Lactose.**—This is never estimated directly, but always by difference, unless adulteration with sugar is suspected, when the water-extract of the curd may be examined polarimetrically or with Fehling's solution to confirm the result by difference.

5. **Total Ash.**—Gently ignite the solid-not-fat in a crucible at as low a temperature as possible or chlorides will be appreciably volatilised.

6. **Salt.**—This is best estimated in another sample of butter. 10 grm. of the butter are weighed into a cylinder, 5 c.c. of chloroform added and sufficient water to make with the water in the butter 50 c.c. Mixed well, without vigorous shaking, and allowed to settle, or, better, separated by rotation. 10 c.c. of the aqueous layer (=2 grm. of butter) are placed in a white porcelain dish, 20 c.c. of water added, the whole roughly neutralised to neutral litmus-paper, and titrated with N/10 silver nitrate, using a potassium chromate indicator. The exact strength of the silver solution should be ascertained against a known weight of sodium chloride.

If the solution is carefully neutralised before titration, the following preservatives, up to the strengths given, do not interfere:

Boric acid, 0.5%; sodium fluoride, 0.5%; salicylic acid, and β-naphthol, sufficient to saturate the aqueous layer.

Colouring Matters.—For the simple distinction between annatto and coal-tar colours, Doolittle's method is recommended (*U. S. Dept. Agric. Bur. of Chem. Bul.* 65, 152). About 2 c.c. of the melted and filtered fat are dissolved in a little ether, in each of 2 test-tubes. Into one is poured an equal volume of dilute (1 : 3) hydrochloric acid, and into the other an equal volume of dilute (1 : 10) potassium hydroxide. The mixtures are shaken well and allowed to stand.

A yellow aqueous layer in alkali tube indicates annatto.

A reddish aqueous layer in acid tube indicates azo-dyes.

For the systematic examination for colouring matters, the following method of Leeds (*Analyst*, 1887, **22**, 150) should be used:

100 grm. of butter are dissolved in 300 c.c. petroleum ether (0.638 sp. gr.) in a separating funnel, the curd and water drawn off, and the ether washed several times with water. The ethereal solution is kept at 0° over-night; it is then poured off from separated glycerides and shaken with 50 c.c. N/10 alkali. The aqueous layer is separated and

titrated with hydrochloric acid till just acid to litmus. The precipitate is filtered, dried, and weighed. If only the identification of the colour be required, less quantities than the above may be taken. To identify the colour, dissolve the precipitate in a few drops of alcohol and test by allowing 1 drop to fall into watch-glasses containing the concentrated acids.

Colour	Sulphuric acid	Nitric acid	Nitric and sulphuric acids	Hydrochloric acid
Annatto	Indigo blue to violet	Blue becoming colourless	Same	No change or brownish.
Turmeric	Pure violet	Violet	Violet	Violet to original colour on evaporation.
Saffron	Violet to cobalt blue changing to red-brown	Light blue to light red-brown	Same	Yellow to dirty yellow.
Carrot	Amber-brown	Decolourised	Same with NO_2 fumes and odour of burnt sugar	No change.
Marigold	Dark olive-green	Blue, changing at once to dirty yellow-green	Green	Green to yellowish-green.
Safflower	Light brown	Partly decolourised	Decolourised	No change.
Aniline yellow ..	Yellow	Yellow	Yellow	Yellow
Martius yellow .	Pale yellow	Yellow, reddish ppt. Magenta at margin	Yellow	Yellow ppt. treated with NH_3 and ignited deflagrates.
Victoria yellow. .	Partly decolourised	Same	Same	Same. Colour returns on neutralisation with NH_3.
[1]Methyl orange .	Pink to brick-red, yellow at edges	Pink and decolourised	Pink rapidly decolourised with NO_2, fumes finally yellow	Pink, the well-known colour with acids.

As slight differences of opinion as to the colours may occur, it is advisable where possible to check them with the actual dye.

A mixture of two dyes is not differentiated, the predominating dye alone giving results as a rule.

Geissler's method (A. O. A. C.) for azo colours: Spread a few drops of the clarified fat upon a porcelain surface and add a pinch of fuller's earth. In the presence of various azo-dyes, a pink to red colouration will be produced in a few minutes. Some samples of fuller's earth act more readily than others.

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[1] Added by writers.

Special oil-soluble, azo-colours (Sudans) are now much used. See A. O. A. C. methods, 1908, p. 195.

Palm Oil.—Recent legislation, especially in the United States, against the sale of butter substitutes containing special colouring matter, has led to the use of highly coloured oils, such as palm oil and fixed oil of mustard. The detection of palm oil has been specially studied by Crampton and Simons (*J. Amer. Chem. Soc.*, 1905, **27**, 270), who have found that tests used for detection of rosin oil are applicable. The following descriptions are from Leffmann and Beam's *Select Methods in Food Analysis*, 2d Ed., 238.

Success in the application of the tests depends on several points: The samples must be kept in a cool dark place until used, filtered at a temperature not above 70°, the heating must be as brief as possible, the testing made promptly thereafter, and the reagents must be pure and colourless.

Halphen's Method.—100 c.c. of the filtered fat are dissolved in 300 c.c. of petroleum spirit and shaken out with 50 c.c. of potassium hydroxide solution (0.5%). The water is drawn off, made distinctly acid with hydrochloric acid, and shaken out with 10 c.c. carbon tetrachloride. The latter is drawn off and part of it tested by adding 2 c.c. of a mixture of 1 part of crystallised phenol in 2 parts of carbon tetrachloride with 5 drops of hydrobromic acid (sp. gr., 1.19). The test is best performed in a porcelain basin and the contents mixed by gentle agitation. Palm oil gives almost immediately a bluish-green.

Liebermann-Storch Method.—10 c.c. of the filtered fat are shaken with an equal volume of acetic anhydride, 1 drop of sulphuric acid (sp. gr., 1.53) is added, and the mixture shaken for a few seconds. If palm oil is present the heavier liquid that separates on standing will be blue with a tint of green (see p. 316).

Preservatives.—Butter is examined systematically for preservatives in the following way:

About 50 grm. are placed in a long tube, 25 c.c. of chloroform added and mixed with the butter. 100 c.c. of 0.1% sodium hydrogen carbonate are added and the whole gently mixed. Vigorous shaking must be avoided. The tube is stood upright until the aqueous layer has separated, or it may be rotated. The aqueous layer is used as follows:

Boron Compounds.—1 c.c. is mixed with 1 drop hydrochloric acid and 8 drops of a saturated alcoholic solution of turmeric, and evaporated to dryness in a porcelain crucible lid. In the presence of 0.02% of *boric acid* the residue is a purple-red, changed to indigo by a drop of strong ammonia (0.880). When boron compounds are not present, the residue is a dirty yellow, and changed by ammonia to a salmon colour.

β-naphthol.—A few c.c. of the aqueous solution are mixed with an emulsion of diazotised naphthionic acid. An *immediate* crimson colour indicates *β-naphthol*, a similar colour being given by *abrastol.*

Pure butter *gradually* develops a rather similar colour.

The reagent is prepared as follows: About 0.2 grm. of 1–4 naphthylaminesulphonic acid is boiled with 10 c.c. of 50% alcohol, cooled (in ice if possible), 1 c.c. of 1 : 3 sulphuric acid added, and then gradually about 1 grm. of potassium nitrite dissolved in about 10 c.c. of water. The suspension gradually becomes yellow. (If the liquid is red the nitrite has been added too fast). The mixture is allowed to stand for 5 minutes, the precipitate filtered and washed with a few c.c. of water. The filter is pierced and the precipitate washed into a test-tube with about 5 c.c. of water. The emulsion so obtained is used as above; 0.02% of *β*-naphthol is easily detected.

Salicylic Acid.—10 to 15 c.c. of the aqueous solution are strongly acidified in a separating funnel with dilute sulphuric acid, and 20 c.c. of ether added and mixed with gentle shaking. The ether is allowed to separate, the aqueous layer run off, the ether washed with 1 to 2 c.c. of water, and then about 10 c.c. of water added with 1 drop of phenolphthaleïn indicator. N/10 sodium hydroxide is run in until, on shaking, the lower layer remains permanently pink. The aqueous layer is run off, N/10 sulphuric acid added equal to alkali used, and the liquid tested with ferric alum solution. A violet colour indicates salicylic acid. Minute quantities (1 : 200,000 can be detected).

Benzoic Acid.—The tube containing the butter-chloroform-water mixture is vigorously shaken and again allowed to settle out (this may be hastened with a centrifuge). The aqueous layer is separated and treated exactly as for salicylic acid, except that neutralisation is effected by a saturated solution of barium hydroxide. The pink aqueous layer obtained is filtered into a small porcelain dish evaporated to 1 to 2 c.c., poured into a test-tube, the colour discharged by a drop or two of very dilute acetic acid, and then a drop or two of neutral ferric chloride solution added. A flesh-coloured precipitate indicates benzoic acid. 0.1% can be detected in this manner, but owing to the solubility of benzoic acid in fat, the following alternative method is recommended for detecting smaller quantities:

About 10 grm. of the butter are boiled for 30 minutes with 10 c.c. of alcohol, and 1 to 2 drops of dilute sulphuric acid, the mixture well cooled, and after pouring off the alcohol into a separator, diluted with water and a few drops of dilute sulphuric acid added, extracted with ether, and finished as above.

Fluorides.—10 c.c. of the aqueous solution are evaporated to dryness in a platinum crucible and ignited gently. The ash is moistened with a few drops of sulphuric acid, and the crucible closed with a watch-glass, coated with paraffin wax, having some scratches made through the wax. Cold water or ice is placed in the watch-glass and the crucible stood on a hot plate for 2 hours. In the presence of fluorides the scratches will be found to be etched on the glass.

If a systematic investigation is not needed, it may be noted that:

Boric acid may be detected as described above, using the water which separates from the butter on melting.

Salicylic acid, if present to the extent of 0.1% may be detected by shaking the melted butter with ferric chloride solution.

β-naphthol, if present to the extent of 0.1%, may be detected by mixing the butter, rendered alkaline by a few drops of sodium carbonate solution, with the diazo-emulsion.

Boric acid may be estimated in the following way: (Richmond and Harrison, *Analyst*, 1902, **27**, 179, and Richmond and Miller, *Analyst*, 1907, **32**, 144.)

25 grm. of butter and 10 to 15 c.c. of chloroform are placed in a stoppered cylinder and sufficient water added to make the total quantity of water present 25 c.c. (the butter as an average may be taken to contain 3.5 c.c. of water). The substances are gently mixed and allowed to stand until separation occurs, or centrifuged. 20 c.c. of the aqueous layer (containing the boric acid of 20 grm. of butter) are pipetted into a 300 c.c. flask, 10 c.c. of a 0.5% solution of phenolphthaleïn in 50% alcohol) added. The mixture is boiled, and titrated while boiling with N/10 sulphuric acid until colourless, and then with N/10 sodium hydroxide until faintly pink. 25 c.c. of glycerol or 2 grm. of mannitol are added and the liquid again titrated until pink. Then if x = c.c. of alkali used for the final titration and y = c.c. required by the glycerol or mannitol used:

$(x-y) \times 0.0062 \times 5 =$ boric acid in %. The factor 0.0062 is given here, but it is advisable to ascertain this against the alkali used.

For the estimation of salicylic acid, see Revis and Payne (*Analyst*, 1907, **32**, 286).

Rancidity.

The question of rancidity of butter as a whole is the one which chiefly concerns the analyst. The causes of this change cannot in the present state of our knowledge be set forth in any definite pronouncement. It has been attributed largely to the growth of micro-organisms and moulds, but light and oxygen play a considerable part in the chain of factors tending to this end.

In the case of butter fat, Laxa (*Arch. f. Hyg.*, 1902, **41**, 119) has certainly shown that species of *Oidium*, *Penicillium*, and *Mucor*, also *Bacillus fluorescens liquefaciens*, effect hydrolysis of the fat, thus forming fatty acids. The volatile fatty acids are in their turn further attacked. It seems that the method of attack is enzymic in its nature.

While in certain forms of rancidity free fatty acids make their appearance and can be estimated in the usual way (page 9), it must not be supposed that rancidity is correctly measured in all cases by the free fatty acidity.

Solstein (*Chem. Rev. Fett. u. Harz. Ind.*, 1905, **12**, 177) has shown that the products causing the characteristic effect of rancidity can be distilled in a current of steam, and finds that the products from rancid lard give strong aldehydic indications, but aldehydes hardly occur in the case of rancid butter. For the detection of rancidity he recommends the application of Welman's phosphoric reagent to the distillate.

In conclusion, it may be said that taste and smell are, so far, the best indicators of rancidity.

Oleomargarin. Margarine.

Substitutes for butter are largely sold under the above names. The better varieties contain as their base "oleo-oil," a product of beef fat. The best portions of the fat are taken from the newly-killed animal, chilled quickly, and rendered at a low temperature. The product, which is called "Premier Jus," is allowed to set slowly to a granular condition, and then, after placing in bags, submitted to hydraulic pressure. The soft portion of the oil is expressed, producing "oleo-oil." The m. p. of the "oleo-oil" can be adjusted to the time of year, by regulating the pressure employed.

This "oleo-oil" is worked up either by itself or with lard, cottonseed oil, coconut, and other oils, according to the grade of margarine desired. The fat is then churned with milk, which has been "soured," after pasteurisation, with a proper butter "starter," a butter colour (annatto in cottonseed oil, or a mixture of annatto and azo-dye) being added to the charge in the churn. The churn mass is cooled with a stream of ice-water, in order to set it, and prevent crystallisation as far as possible. The mass is then thrown on the "worker," salt and a preservative being usually added.

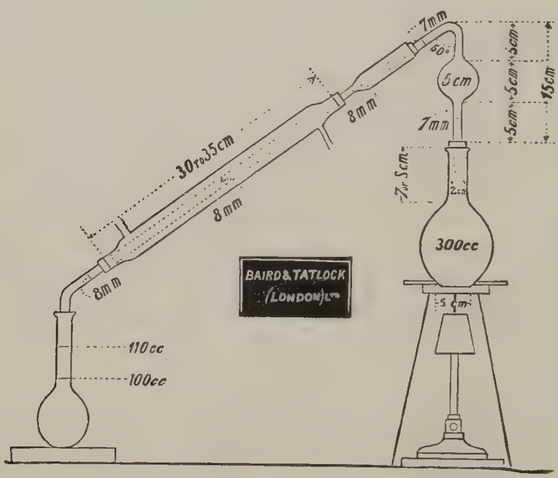

FIG 11.

In England it is illegal to add more than 10% of butter to margarine, and in the absence of coconut and palm-kernel oils, the amount of butter added is controlled by the Reichert-Wollny value of the margarine. As this method must be carried out in a standard way, the following details were laid down by the Government Laboratory and a Committee of the Society of Public Analysts (England): (For details of the A. O. A. C. methods generally used in the United States see pages 23–25. The alkali-glycerol method (p. 25) is quite satisfactory for general inspection work.)

5 grm. of the fat are introduced into a 300 c.c. flask (of the form seen in Fig. 11). 2 c.c. of a sodium hydroxide solution (prepared by dissolving 98% sodium hydroxide in an equal weight of water and protected from absorption of carbon dioxide) and 10 c.c. of alcohol (about 92%) are added, and the mixture heated for 15 minutes under

a reflux condenser, connected with the flask by a T-piece, in a bath of boiling water. The alcohol is evaporated by heating the flask on the water-bath for about 1/2 hour, until the soap is dry. 100 c.c. of hot water which has been boiling at least 10 minutes are added, and the flask heated till the soap is dissolved. 40 c.c. of N/1 sulphuric acid, and 3 to 4 fragments of pumice are added, and the flask at once connected to the condenser as shown. The flask is first heated with a very small flame until the insoluble fatty acids are melted completely without boiling the liquid. The heat is then increased and 110 c.c. are distilled into the graduated flask (within 28 to 32 minutes). The distillate is shaken, 100 c.c. are filtered off, transferred to a beaker, 0.5 c.c. of 1% alcoholic phenolphthaleïn solution added and titrated with N/10 sodium hydroxide or barium hydroxide. A blank test of the reagents is carried out in an identical manner. It should not exceed 0.3 c.c. of N/10 alkali. The volume of N/10 alkali, less the blank, and multiplied by 1.1 is the Reichert-Wollny figure. Operating in this way, the following relations hold fairly well:

R.-W. figure of margarine	Percentage of butter fat present
4.0	10
4.3	11
4.6	12
4.9	13
5.2	14
5.5	15
5.9	16
6.2	17
6.5	18
6.8	19
7.1	20

Arnold gives the following values for margarine, etc.:

	R.-M.	Polenske
Margarine	0.3–0.6	0.48–0.53
Oleomargarine	0.3–0.4	0.48–0.55
Lard	0.2–0.7	0.45–0.55

The following regulations for the control of margarine are in force in various countries (1906):

Canada.—No margarine or butter substitutes to be made or imported.

Austro-Hungary.—Milk and cream may be churned with margarine, but not more than 100 pints by weight of milk (or a corresponding amount of cream) to every 100 pints by weight of fats not butter fat.

In Austria, sesame oil to 10% by weight must be added. In Hungary 0.1 grm. of dimethylamino-azo-benzene must be added to every 100 kilos of margarine.

Belgium.—Margarine may contain 10% of butter and at least 50 parts of sesame oil to be added during churning and 2 parts of dry starch to 1,000 parts of fat.

Sweden.—Margarine must contain 10% sesame oil.

Denmark.—Butter fat in margarine not to exceed 15%. Sodium chloride to be the only preservative and 10% sesame oil to be present.

France.—Not more than 10% of butter fat to be present.

Germany.—Milk and cream may be used as in Austro-Hungary. German law insists that margarine shall contain so much sesame oil that a distinct red colour is produced when 0.5 c.c. of the clear melted fat is mixed with 9.5 c.c. of cottonseed oil, and the mixture shaken with an equal volume of hydrochloric acid and a few drops of 2% alcoholic furfural solution.

Italy.—Margarine is not to be coloured like butter.

England.—Margarine is not to contain more than 16% of water, or more than 10% of butter fat.

Addendum to page 310.

Messrs. S. P. and S. S. Sadtler in a private communication to the American editor report the following results of the application of the Liebermann-Storch test to samples of oils that may b epresent in commercial butter substitutes or in similar substances:

Oil	Colour obtained
Rape	Red to brown
Linseed	Red to brown
Hop	Red to brown
Peanut	Red to brown
Mustard	Green

Mustard oil was easily detected by the test noted by Tolman and Munson; namely, in saponifying with alcoholic solution of alkali, a piece of bright silver is put into the liquid. The metal will be tarnished if mustard oil is present. Mustard oil may be an adulterant of rape oil and thus be found in oils adulterated with the latter.

LARD.

By C. AINSWORTH MITCHELL, B. A. (Oxon), F. I. C.

(See p. 72.) Lard is the fat of the pig, melted and strained to separate tissue and impurities. That known as "bladder-lard" or leaf lard is usually prepared solely from the *omentum* or fat surrounding the kidneys. "Keg-lard" is made from the fat of the entire animal, and usually melts between 28 and 38°, and solidifies between 24 and 31°; hence it melts at a lower temperature than that from the omentum, which has a m. p. of 42 to 45°, and alone has the right to be called lard. The mixed fat from the entire animal would be more appropriately termed "hog-dripping." In the American trade lard is classified into the following grades (Wiley; *Bull.* 13, *U. S. Dept. Agriculture*):

1. **Neutral lard,** rendered from the perfectly fresh leaf of the pig at a temperature between 40° and 50°. It contains about 0.25% of free fatty acids. The best quality is used solely for making oleomargarine, while a second quality, rendered from the back fat, is bought by confectioners.

2. **Leaf lard** obtained by rendering the residue left from 1 at steam-heat under pressure.

3. **Choice Kettle-rendered Lard.**—*Choice lard.*—This consists of fat rendered in steam-jacketed open kettles from portions of the leaf and back fat not used in 1.

4. **Prime steam lard,** rendered by direct steam heat, mainly from the fat of the head, heart, and small intestines, though it may also consist of the fat from any part of the animal.

5. **Guts,** a low quality, which may be derived from any part of the animal except the heart and lungs.

Composition of Lard.—Lard contains the glycerides of stearic, palmitic, myristic, lauric, oleic, and linoleic acids, while Farnsteiner (*Zeit. Untersuch Nahr. Genussm.*, 1899, **2,** 1) has also detected traces of linolenic acid.

The proportion of stearin differs with the origin of the lard. Thus Hehner and Mitchell (*Analyst*, 1896, **21**, 326) found the amounts of stearic acid yielded by fat from different parts of the same pig to range from 15.5% in the flare lard fatty acids to 9% in head fat fatty acids. These differences appeared to be chiefly due to variations in the amounts of the liquid fatty acids. The characteristic differences in the form of the crystals obtained from beef fat and lard in the Belfield test (see below) were attributed by Hehner and Mitchell to a larger proportion of stearic acid in the former; but Kreis and Hafner (*Zeit. Untersuch Nahr. Genussm.*, 1904, **7**, 641) have found that the difference is due to the lard crystals consisting of a mixed ester, heptadecyl-distearin (m. p. 50.5° and 65.2°), whereas beef and mutton fat crystals both consist of palmito-distearin (m. p. 50.5° and 61.6°).

Examination of Commercial Lard.—*The Analytical values* ordinarily obtained in the examination of pure lard are shown in the table on page 72. There are, however, cases of frequent occurrence in which it is difficult to decide whether a sample is genuine though abnormal in its values, or whether it has been skilfully adulterated. Taking into consideration the natural variations in fat from different pigs and from different parts of the same pig, a sample giving abnormal values can only be regarded as suspicious, unless the presence of an adulterating substance be detected by special tests.

Iodine Value.—Lards of American origin are, as a rule, characterised by a considerably higher iodine value than lards of European origin. Thus of 100 samples of American lard examined by Voigtländer (*Zeit. angew. Chem.*, 1898, 857) no fewer than 88.5 had an iodine value of 61 to 66, while in 41 cases the value exceeded 64. On the other hand, Dieterich who examined 112 samples of German lard, obtained iodine values of 48 to 53 with 71.7%, while only in 2 cases was the value as high as 64.

An estimation of the iodine value and of the stearic acid by Hehner and Mitchell's method (p. 393) in the mixed fatty acids of a lard may, when considered together, sometimes give useful indications of adulteration with beef fat and a vegetable oil. Samples of lard, believed to be genuine, examined by Hehner and Mitchell gave the following results:

Iodine values,	61.2	57.5	61.2	65.6	63.6
Stearic acid, %,	13.0	16.0	6–7	9.9–10.6	7.4

A high iodine value (*e. g.*, 65), in conjunction with a high proportion of stearic acid (*e. g.*, 15%) would point to the sample having been "stiffened" with beef stearin and then rendered sufficiently fluid by an addition of cottonseed or other vegetable oil.

The Bromine Thermal Value.—This corresponds closely with the iodine value in the case of lards, and the method described on page 60 affords a very rapid means of determining the halogen absorption of a sample.

The Iodine Value of the Liquid Fatty Acids.—Since vegetable oils contain fatty acids of a greater degree of unsaturation than the fatty acids in lard, the iodine value of the liquid fatty acids separated by the lead-ether method (p. 390) may afford useful evidence of adulteration. Results thus obtained with different grades of lard and with vegetable oils are given by Wallenstein and Fink (*Chem. Zeit.*, 1895, **18**, 1189) and by Lane (*J. Soc. Chem. Ind.*, 1901, **20**, 1083). The liquid fatty acids of pure lard usually give an iodine value of 95 to 97 (American lards up to 115), while the corresponding value in the case of cottonseed oil is about 146.

Refractometer Reading.—The results obtained with the butyro-refractometer or oleo-refractometer approximate roughly to the iodine value; and, like that constant, differ with the part of the animal from which the fat was obtained. Thus, a typical European lard with iodine value of 59 gave an oleo-refractometer reading of −12.5°, while an American lard with iodine value of 65 gave a reading of −4.0° in the oleo-refractometer.

Results obtained with lards and substances used to adulterate them are given by Jean (*Bull. Soc. Chim.*, 1895, **13**, 780) and by Dupont (*ibid.*, 775). The method may be found useful as a preliminary sorting test.

Solidification-point of Fatty Acids.—This differs much with the origin of the fat. Thus, fatty acids from the ham and head fat, solidified at 34.8° and 34.6°, respectively, while those from the flare of the same pig solidified at 40.0° (Hehner and Mitchell). Still, this value (by Dalican's method), considered in conjunction with the iodine value, may, in some cases, afford confirmatory evidence of adulteration.

Acidity.—The proportion of free fatty acids in lard, when freshly rendered, is usually below 0.5% (as oleic acid). Twelve samples of American lard examined by Wiley contained from 0.35 to 1.0%.

Water.—As a rule, the amount of water is insignificant. Thus, in the case of American lards the proportion found by Wiley ranged from a trace to 0.7%. A rapid method of ascertaining the amount of water was based by Polenske (*Arb. a. d. Kaiserl. Gesundheitsamte*, 1907, **25,** 505) on the temperature at which the melted fat becomes turbid. This has recently been confirmed by Fischer and Schellens (*Zeit. Untersuch. Nahr. Genussm.*, 1908, **16,** 161), who obtained the following results in substantial agreement with the figures of Polenske:

Water, %	0.45	0.40	0.35	0.30	0.25	0.20	0.15
Turbidity temperature,°.	95.2	90.8	85.0	75.8	64.6	53.2	41.2

Of the samples of German lard examined by Fischer and Schellens, none contained more than 0.3% of moisture, and, in their opinion, therefore, lard should not show a turbidity temperature exceeding 75°.

The method is not applicable to the determination of moisture in tallow or beef fat.

In the case of lard adulterated with water, the latter may be estimated by heating 10 grm. of the sample at 110° until no more globules of water are seen, and ascertaining the loss in weight. This form of adulteration is no longer of frequent occurrence.

Detection of Vegetable Oils.—When a consideration of the analytical values (notably the iodine value) of a sample of lard indicates the probable presence of a vegetable oil, further evidence may be obtained from the iodine value of the liquid fatty acids, as mentioned above.

The *phytosteryl acetate test* (see page 301) may then be used for further proof, and special tests may be applied for the detection of the vegetable oils most likely to be present. These are *cottonseed oil* and *cottonseed "stearin," sesame oil, maize oil, arachis oil* and *coconut oil.*

Cottonseed oil and stearine may be detected by the silver nitrate test, Halphen's test and the nitric acid test (see *Cottonseed Oil*, page 136).

Sesame oil may be detected by the furfural test, Soltsien's test and Tocher's test (see *Sesame Oil*, page 141).

Maize Oil.—No distinctive colour test for this oil has been discovered. Its presence in lard will be indicated by the phytosteryl acetate test, the high iodine value of the liquid fatty acids, a high yield of linolic tetrabromide on brominating the liquid fatty acids, and the negative results of characteristic tests for the other oils. The Reichert-Meissl value may also afford confirmatory evidence (see *Maize Oil*, page 139).

Arachis oil is best detected by a determination of the arachidic acid by Renard's method (see *Arachis Oil*, page 91).

Coconut oil will be indicated by the increased saponification value and the Reichert-Meissl value (see also *Coconut Oil*, page 187, and *Butter*, page 279).

In drawing conclusions as to the adulteration of a lard with cottonseed or sesame oil, it should be remembered that indications given by the special colour tests may possibly be due to the pigs having been fed upon cottonseed or sesame oil-cake. Thus, Soltsien (*Chem. Zentralbl.*, 1901, **1**, 539) found that many American lards gave a faint colouration in Halphen's test for cottonseed oil similar to that which would have been produced by an addition of about 1% of that oil; while Dunlop (*J. Soc. Chem. Ind.*, 1906, **25**, 459) found that fat from the back and shoulder of a pig fed upon cottonseed cake gave indications in the test corresponding to no less than 10%. The iodine value of the fat, however, was quite normal. (See p. 301.)

Beef Fat and Other Animal Fats.—Some indications of the presence of beef or mutton stearin in lard may be afforded by a determination of the m. p. of the fatty acids and of the proportion of stearic acid which they contain, especially when considered in conjunction with the iodine value and the results of special tests for vegetable oils.

Crystallisation of the Fat.—A qualitative test for the presence of beef fat was described by Belfield (*Analyst*, 1888, **13**, 70). When the fat is dissolved in ether, and the solution allowed to evaporate spontaneously in a test-tube closed with a little cotton-wool, crystals are obtained which, examined under the microscope, appear broad with chisel-shaped ends in the case of lard, but needle-shaped and grouped in fan-like bunches when derived from beef or mutton fat. Kreis and Hafner (*supra*) have shown that the difference is due to the crystals consisting of different mixed glycerides. In the case of the flare lard recrystallisation as advocated by Stock (*Analyst*, 1894, **19**, 2) tends to give crystals approximating in general form to those obtained from beef fat (Hehner and Mitchell, *supra*).

When a mixture of lard and beef fat is crystallised in this way, the form of the crystals is intermediate between those from the respective ingredients, though approximating more toward the form of the lard crystals.

Again, Dunlop has shown (*loc. cit.*) that when the "plumose" crystals from beef or mutton fat are recrystallised, they finally show numerous individual, flat, chisel-ended crystals closely resembling those obtained in a first crystallisation from lard. Moreover, since the first crystals from beef fat are more soluble than the first crystals from lard, recrystallisation of a mixture of the two from ether (as in Stock's method) will not effect a concentration of the beef stearin.

Stock's Process (*Analyst*, 1894, **19**, 2) is a quantitative application of the Belfield test. The deposits obtained on crystallising the fat under fixed conditions are washed with definite quantities of ether at a definite temperature, and weighed. The results are then compared with those obtained under the same definite conditions from standard mixtures of lards of different m. p. with different proportions of beef stearin.

In the light of the experiments of Hehner and Mitchell (*Analyst*, 1896, **21**, 328) and of Dunlop (*loc. cit.*), further investigation of the nature and behaviour of the deposits from mixed fat appears necessary before trust can be placed in the results of this test.

With regard to the original qualitative test, Dunlop has shown that it is necessary to examine the crystals under a magnification of 300 to 400 diameters to see the form of individual crystals, and not to rely solely on the fan-like grouping of the bunches of crystals, as seen under a magnification of 100 diameters as a proof of the presence of beef stearin.

At its best, the test can, as yet, only be regarded as affording confirmatory evidence of adulteration; and, as was pointed out by Hehner (*Analyst*, 1902, **27**, 24), the occurrence of the "beef-form" of crystals should only be regarded as a proof of the presence of beef or mutton fat when the presence of a vegetable oil has been detected and the lard has a high iodine value.

LINSEED OIL.

By C. A. KLEIN, Chemist,

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(See p. 70.) **Linseed oil** is obtained from the seeds of the flax (*Linum usitatissimum* L). The plant has an exhausting effect on soil, which necessitates some local adjustment and change of the source of supply.[1] Linseed is principally imported from the Baltic ports, Russia, East India and South America, and is to some considerable extent cultivated in various parts of Europe, Egypt, and Brazil. Linseed growing experiments have recently been carried out in New South Wales and have been attended with considerable success. Large quantities of linseed are grown in North America, though little of this is exported.

Commercial linseed is never pure, being contaminated by foreign seeds, owing to various plants grown with the flax. This fact is recognised by the trade and the Linseed Association which samples and tests all seed imported to England bases its valuation on the amount of foreign seeds present, half value being allowed for oleaginous seed other than linseed, while non-oleaginous seed is not given any value. Baltic seed is freest from foreign matters and hence the oil expressed from it is the purest. In certain Black Sea ports it was the practice to add 5% of hemp or ravison seed, but this has been discontinued. The foreign seeds usually present are hemp, mustard, rape and cameline, the exact variety or combination depending on local conditions. According to Wijs,[2] La Plata seed seldom contains more than 5% of foreign seed (mostly non-oleaginous). Indian seed rarely contains more than 6%; one Calcutta grade, however, has been examined which contained as much as 30%. South Russian seed is fairly pure, while North Russian seed has been found to contain from 5 to 10%, and even 20% of foreign seeds. Wijs (*loc. cit.*) has determined the iodine values of a large number of samples of oil from mixed and unmixed seed from various sources. It has been shown that linseed from different localities carefully freed from foreign seed yields an oil quite equal to that from Baltic seed. The superiority of Baltic oil is entirely due to the more careful harvesting. The foreign seeds usually affect the drying qualities of the oil. Linseed varies in size and colour. The usual colours are a purplish-brown, and a reddish-brown, but a white variety is known. This variety is grown in some parts of the North-West Provinces of India, but no care is taken to keep the strain pure. According to Church,[1] the seed contains 45% of oil, the product obtained from a picked sample being nearly colourless.

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[1] Leather. *Mem. Dept. Agriculture in India*, 1907, 1, 13.
[2] *Chem. Rev. Fett-Harz-Ind.*, 1899, 6, [2], 29.

Leather (*loc. cit.*) describes experiments carried out in India with regard to the effect of transference of rich seed to localities which usually produce a seed of low oil content; the results show a reduction in the percentage yield under these conditions.

Preparation of Oil from Seed.—The percentage of oil obtained from a given variety of seed cannot be said to be constant, as the yield is influenced by conditions of soil, climate, ripeness, seasons, etc.

Schindler and Waschata[2] found in 43 samples of linseed oil from 35.74 to 43.26% of oil, an average of 39.48. The following table, showing the oil contents of seed from different sources, is due to them.

Kind	Oil in %	Average
Calcutta	38.55–43.26	40.16
Bombay	36.96–42.90	41.03
Russia	36.53–39.06	37.96
Mamara	....	41.27
Constanza	38.00–38.94	38.47
Levant	36.95–42.04	40.04
Hungary	36.63–37.86	37.13
Morocco	35.74–39.75	37.74
North America	....	36.41
La Plata	36.45–39.18	37.59

Extraction with ethyl ether yields larger quantities of crude oil than is obtained by using petroleum ether.

Leather[3] has examined seeds of Indian origin, and by a process of double extraction using ethyl ether has found the oil contents of different seeds vary from 35.60% to 43.80%. The double extraction consisted in first extracting the bulk of the oil, then drying and crushing the residue before a second extraction. This method gave values 3% higher than by single extraction.

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[1] Chemistry of Paints and Painting, 1901.
[2] Benedikt and Ulzer. *Analyse der Fette, etc.*, 1908.
[3] *J. Soc. Chem. Ind.*, (Abstract) 1907, 26, 622.

According to Andes,[1] linseed contains 8% of water, 33% oil, 25% of albuminoid matter, traces of tannin, 4 to 5% of ash. When linseed is cultivated for oil only, a larger yield is obtained than when fibre has been desired—in the latter case the seed is not ripened sufficiently, and therefore does not possess the full oil content.

The seed is kept from 2 to 6 months before pressing, as new seed yields a turbid and more viscous product containing much mucilage. The oil expressed from American and Russian seed usually contains a larger proportion of moisture than Calcutta and East Indian seed which is invariably full-grown and matured, and consequently gives a greater yield of oil.

The extraction of oil from seed is carried out by one of the following methods:

1. Cold pressure, yield 20%–21%.
2. Hot pressure, yield 27%–28%.
3. Extraction with various solvents, yield 32%–33%.

1. *Cold pressure* gives a light coloured golden-yellow product, which is not unpleasant to the taste. In some parts of Russia, India, and Germany it is considered edible; further it contains less solid glycerides and consequently is a better drying oil.

2. *Hot pressure* gives a darker coloured product, having an acrid flavour, which renders it only suitable for technical purposes.

3. *Extraction*, which is not extensively practised in England. Mitarewski[2] states that oil extracted by the usual solvents, benzene, carbon disulphide, carbon tetrachloride and naphtha, lacks the characteristic smell of linseed or pressed oil. In the case of carbon disulphide extraction, the oil has a strong smell of garlic, and a dark reddish colour, while oil extracted by other solvents is of a yellowish-green colour. Solvents do not cause any determinable alteration in the oil or cake, except carbon disulphide, which increases the quantity of volatile acids—hence high saponification values result. Toch[3] states that the solvent is liable to extract proteids from the seed, thus decreasing its value as a food, and he advises examination of oil for

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[1] Vegetable Fats and Oils, 1902.
[2] *J. Soc. Chem. Ind.*, 1906, **25**, 818.
[3] Technology of Mixed Paints, 1907.

nitrogen in order to ascertain whether it is extracted or, as he terms it, "new process" oil.

According to Petit,[1] extraction yields a product containing all the fats present in the seed, some of which do not dry.

Fassbender and Kern[2] have shown that it is possible to obtain a pure oil from an impure seed, as the cake retains a large proportion of the foreign oils.

Linseed Cake.—The press cakes obtained by the pressing of linseed furnish a very valuable cattle food which retains about 10% of the oil. The cake obtained by the extraction process is of little or no value as food.

According to the researches of Dunston,[3] Henry,[3, 4] and Auld,[3, 4] linseed cake contains a cyanogenetic glucoside "linamarin" together with an enzyme which occurs naturally in the flax plant and in linseed. In the ordinary process of hot pressing the temperature is high enough to destroy the enzyme, but with cold pressure the enzyme is active, and in the presence of water acts on the glucoside with the production of hydrocyanic acid. It is suggested that cases of cattle poisoning previously considered to be due to the presence of foreign seeds might be explained by this enzyme action.

Refining.—The varieties of linseed oil usually recognised in commerce are "Raw," "Refined," "Artists'," and "Boiled." The latter is dealt with in a subsequent chapter.

Raw linseed oil varies in colour from amber-yellow to yellowish-brown and has frequently a greenish fluoresence, and a somewhat sweet, sickly odour. In the refining process these two characteristics are removed. According to Toch (*loc. cit.*), the colouring of linseed oil is usually due to chlorophyll, or, as occasionally happens when a reddish cast is observed, to erythrophyll; and bleaching depends on the conversion of these colouring matters into yellow xanthophyll.

For ordinary refining, the process generally adopted is that of agitating the raw oil after a preliminary settling and heating, which causes the coagulation of impurities, with 1%–2% of sulphuric acid (sp. gr. 1.845) in lead-lined tanks. The charred mass formed by the acid carries down the bulk of the impurities, and after again being allowed to settle the oil is drawn off and washed by boiling with water. After settling, the water and "foots" are run off from the refined oil. Linseed oil is usually stored in lead-lined tanks, in which a further deposit of mucilage or "foots" takes place. These foots are used in the manufacture of soap, putty, or low-grade paints.

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[1] White Lead and Zinc Paints, 1907.
[2] *Zeit. angew. Chem.*, 1897, 331.
[3] *Proc. Roy. Soc.*, 1906, B, **78**, 145.
[4] *J. Soc. Chem. Ind.*, 1908, **27**, 428.

Kochs[1] states that the mucilage in linseed husks is a carbohydrate formed from starch during the ripening of the seed. It behaves like starch and is partly converted into glucose on heating with dilute acid. Kochs heated a portion of "foots" with 25% hydrochloric acid for 10 minutes and, after neutralising with caustic soda and boiling the filtrate with Fehling's solution, obtained a precipitate of cuprous oxide corresponding to 16.3% of linseed mucilage. Another sample of foots from Indian seed contained nitrogen corresponding to 11.3% proteids and 9.1% ash.

Bleaching by means of hydrochloric acid and dichromates is also adopted. This method yields a product very pale in colour, which frequently has a very characteristic odour. If the process is not carried out with care, there is danger of chlorinating the oil. (See paragraph on Iodine Values.)

A very large number of processes have been patented for refining linseed oil, among which may be mentioned filtration through Florida earth or charcoal, treatment with tannin, aluminium hydroxide, zinc chloride, ozone, treatment with peroxides of calcium, magnesium, etc., and sulphuric acid, the oxygen liberated by the latter causing bleaching. None of the foregoing call for any special mention.

In the preparation of artists' oil, raw oil is allowed to stand for weeks or even months to cause impurities to settle, and is then treated with litharge or lead acetate. It is then bleached by exposure to sunlight. Various secret methods are also employed. Iron or zinc sulphates are also used, and are said to hasten the deposition of impurities.

Technical Applications.—Linseed oil is the most important of the drying oils, and finds extensive application in the following industries: paints, varnishes, oil and leather cloth, linoleum, printing ink, rubber substitutes, etc.

The selection of linseed oil for varnish is a question of importance, and much care has to be exercised in order to obtain the best results. There is a general preference for Baltic oil and, as a consequence, Baltic oil is usually at a premium. Bearn states that Baltic oil stands its colour much better on heating, hence the preference for Baltic oil in varnish-making; also it is "harder" and does not tend to deposit mucilage or break on standing. For varnish-making it is essential that the oil should be free from mucilage, which, as previously stated, is deposited on standing. Metallic lead appears to hasten the deposition, hence the practice of storing oil in lead-lined vessels. Thompson[1] has investigated this question, and has found that the formation of mucilage or coagulation of oil is due to the presence of phosphates and sulphates. Thompson has examined the "mucilage," "spawn," or "break," and after removal of oil by petroleum-ether found it to contain 47.79% of ash, which, on analysis, showed 20.96% CaO, 18.54% MgO, 59.85% P_2O_5, and traces of sulphate. It will be seen that storage effects the removal of those substances which render oil unsuitable for varnish-making. (See paragraph on Ash.)

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[1] *Oil and Colourman's Journal*, 1906, 29, 1882.

Niegmann[2] states that linseed oil to be used for varnish, boiled oil, linoleum, etc., should not form flocks when quickly heated to boiling in a test-tube. Also that only oils which do not give any deposit on standing for a long time, which assume a clear greenish colour on boiling, and do not show turbidity on standing when exposed to air for a month should be used. (See Lippert, *Zeitsch. angew. Chem.*, 1897, 306.)

Raw oil, intended for making pale boiled oil or varnish, should not have a sp. gr. below 0.935, otherwise it will probably contain a proportion of other seed oils which will impair its drying qualities; 3% of such admixture is the maximum allowable in linseed to be used for producing oil for varnish work.

In practice, the best oil is that which dries most perfectly, but the rapidity of drying and the condition of the ultimate product are important factors to be considered in judging its quality. Thus the dried oil may be tough, very elastic, hard and brittle, or rotten. An oil giving a hard product is to be preferred, as elasticity can be readily imparted in the after-treatment if required.

Extraction from Paint.—Linseed oil (both raw and boiled) is the most generally employed vehicle for paint. For high-class work, as in artists' colours, poppy seed and walnut seed oil are frequently used. It can be readily extracted therefrom by the use of any ordinary solvent. In some cases extraction may not be complete owing to reaction having taken place between the oil and the pigment, *cf.* Davis and Klein (*J. Soc. Chem. Ind.*, 1907, **26**, 848), who found a small quantity of unextractable fatty matter in white lead, probably due to the combination of the free fatty acids of the oil with white lead.

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[1] *J. Amer. Chem. Soc.*, 1903, **25**, 716.
[2] *Chem. Zeit.*, 1905, **29**, 465.

In the examination of a mixed paint, the light oils may be distilled off in steam, and the residual oil extracted. It must be pointed out that it is by no means unusual to obtain values from an extracted oil quite different from those of the original oil used, *cf.* Boettinger, *Chem. Zeit.*, 1899, **12**, 22; Lotter, *J. Soc. Chem. Ind.*, 1895, **14**, 169. Also see paragraph on Iodine Values.

In some cases it is found difficult to free the solution in ether from the solid matter owing to the finely divided pigment being held in suspension. If filtration fails, a centrifuge must be used, and this is usually most effective.

The extraction of linseed oil is best carried out by shaking the paint with the solvent, then allowing the pigment to settle, and evaporating a portion of the clear solution in a tared vessel. It is to be noted that the quantities of oil required by different pigments to produce a paint of similar consistence differs considerably.

Substitutes.—There are no substitutes for linseed oil in general use in England. Various substitutes for painting work have been patented, but these have not so far met with approval.

In America, according to Holley and Ladd,[1] cottonseed oil, although seldom found in house paints, is often used in barn paints.

Composition.—The elementary composition of linseed oil is given by different authorities as below.

Source	Composition			Observer
	C	H	O	
Cold drawn	78.11	10.96	10.93	Schädler.
Hot drawn	75.27	10.98	13.85	
Not stated	77.57	11.3	11.10	Cloez.
Not stated	75.21	10.71	14.08	Williams,[2] Mean of 2 estimations.
Extracted from Baltic seed by petroleum ether.	76.24	10.63	13.13	Bearn.

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[1] Holley and Ladd. Mixed Paints, etc., 1908.

[2] *Analyst*, 1898, **23**, 253.

Church (*loc. cit.*) states that oil extracted by carbon disulphide contains more oxygen and less carbon than oil obtained by pressure.

The chemical composition of linseed oil is not completely understood. The following figures are quoted, but the reader is referred to Lewkowitsch (*loc. cit.*) for a résumé of present views together with the references to original papers.

Linseed oil contains:

10%–15% glycerides of solid fatty acids;
i. e., stearic, palmitic, and myristic.
85%–90% liquid glycerides.

Hazura and Grussner state that the fatty acids from the liquid glycerides consist of

Oleic acid	5%
Linoleic acid	15%
Linolenic acid	15%
Isolinolenic acid	65%

Fahrion gives the following:

Unsaponifiable matter	8.0%
Combined fatty acids—palmitic and myristic acids	8.0%
Oleic acid	17.5%
Linoleic acid	26.0%
Linolenic acid	10.0%
Isolinolenic acid	33.5%

See

Fokin. *Chem. Centr.*, abstr., 1902, 2, **8,** 601.

Tolman and Munson. *J. Amer. Chem. Soc.*, 1903, **25,** [3], 960.

Fahrion. *Zeits. angew. Chem.*, 1903, 1193.

Fahrion. *Ibid.*, 1904, 1484.

Haller. *Compt. rend.*, 1906, **146,** 259.

Fokin. *J. Soc. Chem. Ind.* (abst.), 1906, **25,** 935.

Bedford. "Ueber die ungesättigten Saüren des Leinöls," *Inaugural Dissertation*, Halle a/S., 1906.

Erdmann and Bedford. *Ber.*, 1909, **42,** 1324.

Bedford and Rispe. *Ibid.*, 1334.

Specific Gravity.—The sp. gr. is usually 0.935 at 15°, but may range between 0.931 and 0.937, depending on source, age, exposure, and method of refining.

See table of constants, and general chapter on sp. gr. Ballantyne[1] has investigated the influence of exposure to light and air on linseed oil.

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[1] *J. Soc. Chem. Ind.*, 1891, **10,** 30.

He found that linseed oil which was exposed to sunlight and air and agitated every morning behaved as below:

	1 month	2 months	3 months	4 months	5 months	6 months
Sp. gr. at 15.5°...	0.9321	0.9336	0.9353	0.9359	0.9372	0.9385

The original sp. gr. was 0.9325.

In a corked bottle, that is excluding exposure to air, there was practically no change, *i. e.*, from 0.9325 to 0.9327 in 6 months.

Ballantyne found a decrease in sp. gr. of linseed oil kept in the dark, although exposed to air and agitated daily.

Bellier[1] records 0.930 as the sp. gr. of a sample of edible linseed oil.

Wijs[2] found that the sp. gr. of linseed increases with its iodine value. Thus he found that samples, the sp. gr. of which increasep from 0.9310 to 0.9352, had iodine values ranging from 180.1 to 200. This can only apply to fairly new samples, as it has been observed by Ballantyne that on exposing a sample of oil to air and light, the sp. gr. increases, while the iodine value is lowered.

Solidification.—According to Chateau, linseed oil solidifies at —27° into a yellowish mass.

Lewkowitsch (*loc. cit.*) states that at —25° "stearine deposits."

Sjollema[3] states that linseed oil remains liquid when cooled below 0° and in this respect differs from most other oils. If free fatty acids are present, crystallisation may occur. Certain varieties of linseed oil, *e. g.*, North Russian, will remain clear at —14°, and can be mixed with several per cent. of cottonseed oil, and then will only show the same turbidity temperature as genuine linseed oil from other sources.

Flash-point. According to the *Oil and Colourman's Journal*,[4]

La Plata flashes at......................	450° F. (close)
Calcutta flashes at	490–500° F. (close)
Baltic flashes at over....................	500° F. (close)

Künkler[5] quotes linseed oil sp. gr. 0.930, flash-point 285° (open test). M. Rakusin[6] states that linseed oil, sp. gr. 0.930–0.935, flashes at 20.5–22.5°, and points out that adulteration by mineral oil is readily detected by a lowering of the flash-point.

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[1] *Ann. Chim. anal.*, 1905, **10**, 52.
[2] *Chem. Rev. Fett-Harz-Ind.*, 1899, **6**, 29.
[3] *Zeitsch. Nahr. Genussm.*, 1903, **6**, (14), 631.
[4] 1901, **22**, 2081.
[5] *J. Soc. Chem. Ind.*, 1890, **9**, 197.
Chem. Zeit., 1905, **29**, 690–691.

Bearn (private communication) gives the following figures showing flash-point of linseed oil and of mixtures of linseed oil with mineral oil:

	5% mineral oil	10%	20%	50%
East Indian oil, flash-point 472° F.	464	455	450	418
Baltic linseed oil, flash-point 470° F.	460	455	448	420

Ash.—The ash of raw or refined linseed oil is seldom determined. The Russian official[1] test fixes 0.75% as the maximum ash, permissible in boiled oil.

Thompson[2] has determined the ash in samples of oil, and obtained the following results:

1. Fresh double filtered raw American linseed oil, 0.1429% ash.
2. Fresh double filtered raw American linseed oil, 0.1967% ash.
3. Good well settled oil, 0.0609% ash.
4. Best American linseed varnish oil, traces.

Lewkowitsch has examined linseed oils containing 0.2% of ash and states that such oils deposit considerable quantities of mucilage.

Brannt[3] gives the following analyses of ash:

	From linseed	From linseed cake
Potash	28.80	25.24
Soda	1.66	1.64
Magnesia	13.63	14.40
Lime	8.59	8.45
Ferric oxide	2.03	3.52
Chlorine	0.06	1.31
Sulphuric acid	0.10	1.68
Silica	0.40	1.81
Phosphoric acid	44.73	41.98

Solubility.—Linseed oil is very soluble in acetone, petroleum spirit, ethyl ether, carbon disulphide, chloroform, carbon tetrachloride, turpentine, benzene, and petroleum. Petroleum spirit, acetone, ethyl ether are usually used for the extraction of paints. It dissolves in about 5 parts of boiling and in 40 parts of cold absolute alcohol.

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[1] *Oil and Colourman's Journal*, 1905, **28**, 1497.

[2] *J. Soc. Chem. Ind.*, 1903, **22**, 1005.

[3] Animal and Vegetable Fats and Oils, 1896.

Free Fatty Acids.—The amount of free fatty acids present in linseed oil is low, usually ranging from 0.5 to 4%.

Nordlinger[1] and Thomson, and Ballantyne[2] have, however, examined samples containing free fatty acids ranging from 0.41 to 4.19%. According to Lippert,[3] "livering of paints" is due to the presence of free fatty acids. The proportion of free acids increase with age. A sample of raw Baltic linseed oil (33 years old) examined by Bearn, contained 12.45% free fatty acids. The sample had a very rancid taste. (See note on linseed soap stock.)

Unsaponifiable Matter.—Thomson and Ballantyne[4] found oil from various sources to contain 1.09 to 1.28%. Williams[5] found 0.8 to 1.3% in raw oil, and 1.3 to 2.3% in an oil boiled at a high temperature. He is of the opinion that any oil containing more than 2.5% must be considered as adulterated. He also states that low temperature boiling does not affect the amount of unsaponifiable matter.

Fendler[6] states that the normal amount of unsaponifiable matter does not exceed 2.0% and that blowing or oxidation does not increase the amount. Linseed oil obtained by pressure does not contain more unsaponifiable matter than that obtained by extraction. He recommends the determination of the mineral matter by the iodine absorption of the unsaponifiable matter, and states that the unsaponifiable matter of linseed oil is usually solid. According to Niegeman, the iodine value of the unsaponifiable matter does not vary greatly; further, the value is not decreased by exposure of the unsaponifiable matter to air in the dark, though light is fatal. When dried to a skin, no iodine value is obtained.

Niegeman[7] found in 18 samples a maximum value of 2.15%, and a minimum of 0.74%—an average of 1.35%, the average being exceeded in 7 samples. In view of these figures, he suggests that it is unfair to condemn an oil solely because its unsaponifiable matter exceeds 1.3%.

Thoms and Fendler[8] fix 2.0% as limit, and state that exposure to light and air, or even breaking the oil, does not increase this value. The value is only increased when the linseed oil has been dried to a varnish, and there is a reduced iodine value. The proportion of unsaponifiable matter is not less in extracted oil than in oil obtained by pressure (confirming Fendler) thus 1.09% in pressed oil, and 1.24% in oil extracted by ether from the same seed.

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[1] *J. Soc. Chem. Ind.*, 1889, **8**, 806.
[2] *Ibid.*, 1891, **10**, 236.
[3] *Zeitsch. f. angew. Chem.*, 1897, 779.
[4] *J. Soc. Chem. Ind.*, 1891, **10**, 336.
[5] *Ibid.*, 1898, **17**, 305.
[6] Ber., 1904, **37**, 294.
[7] *Chem. Zeit.*, 1904, **28**, 97.
[8] *Ibid.*, 1906, **30**, 832.

Thomson and Dunlop[1] found, in 5 samples, unsaponifiable matter ranging from 0.88 to 1.25%, average 1.12%.

As the result of 150 estimations Bearn found an average of 1.2% unsaponifiable matter; only in rare cases did the figure exceed 2%.

Saponification Value.—Wright and Mitchell[2] quote values ranging from 183 to 221, while Lewkowitsch[3] gives 190 to 195.2.

Iodine Value.—Many of the earliest recorded iodine values are far too low, viz., about 150. This is due to the fact that the proper conditions for the estimation had not been ascertained. By the adoption of proper methods perfectly satisfactory results are obtained, and this value is one of the most characteristic tests for identification purposes, though discretion must be used in interpreting low figures.

Linseed oil (raw and refined) has been found by various workers to have an iodine value varying from 165 to 200, the average values being 175 to 190. These values are higher than those of any fatty oil other than perilla oil.

The highest iodine value on record appears to be that obtained by Thomson and Dunlop,[4] who found 205.4 to be the value of a sample of oil expressed from Riga seed. The following figures due to Thomson and Dunlop show that an apparent relationship exists between the iodine value and the refractive index.

Source	Iodine value. Wijs	Zeiss refractometer reading at 25°
Linseed oil (Riga)	205.4	85.5
Linseed oil (St. Petersburg)	200.0	84.2
Linseed oil (North American)	194.6	83.2
Skate liver oil	191.1	82.5
Linseed oil (Calcutta)	188.6	81.7
Haddock liver oil	186.4	81.0
Linseed oil, river plate	185.5	81.0
Whiting liver oil	184.2	81.0

The above figures show a close resemblance between liver oils and linseed oil. Thomson and Dunlop consider that Wijs' method gives higher figures than Hübl, and that when a sample of linseed oil is found having a value lower than 180, as estimated by the former method, a searching investigation should be carried out as to its purity.

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[1] *Analyst*, 1906, **31**, 281.
[2] Animal and Vegetable Fixed Oils and Fats, etc., 1903.
[3] Chemical Technology and Analysis of Oils and Fats, 1904.
[4] *Analyst*, 1906, **31**, 281.

Lewkowitsch fixes 170 as a minimum.

The following notes will be found of value in the interpretation of low iodine value in genuine linseed oil:

1. The writer has encountered samples of linseed oil having as low an iodine value as 154.5. On inquiry, this was found to be oil bleached by means of hydrochloric acid and sodium dichromate. It was very pale in colour and had a characteristic smell. From this low iodine value, it was evident that chlorination had taken place during bleaching. Further samples examined by the writer gave:

Before bleaching	173.0
After bleaching	166.4

It is, therefore, evident that with care serious chlorination can be avoided. The ordinary process of refining by means of sulphuric acid does not appreciably affect the iodine value.

2. When linseed oil has been exposed to air and light, a lowering of the iodine value is observed. This is due to absorption of oxygen.

Ballantyne[1] found that linseed oil exposed in a bottle to light and air, and agitated daily, behaved as below. The writer has confirmed this observation, and the results are given together.

Source of sample	Original value	After 1 month	After 2 months	After 5 months	After 6 months	Observer
Not known	173.46	171.8	171.78	169.07	166.17	Ballantyne
Source	Original value	Kept in dark	Exposed to light	Exposed to light with lead	Period	
East Indian Refined	175.0	174.5	170.0	165.6	2 months	Klein

The greater decrease when using a vessel containing lead is of interest. The strips of lead became coated with a deposit which was insoluble in ether. After removal of oil by ether the product was a white powder, melting at 103.5 to 104.5°. Bleaching took place in the vessels exposed to sunlight, but the bleaching effect was not increased in the vessel containing the lead.

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[1] *J. Soc. Chem. Ind.*, 1891, 10, 31.

The effect of boiling on the iodine value is shown in the section on boiled oil.

3. Linseed oil which has been extracted from a paint is frequently found to have low iodine values. Boettinger[1] found that linseed oil, having an original iodine value of 183.3, altered when ground with white lead—after 17 days—to 131.0; and to 122.17 after 2 months. Whiting and ochre showed the same changes.

The iodine value of a sample is a fairly good indication as to its drying properties. Fox has shown that the oxygen absorption of an oil bears a relationship to the iodine value. This relationship is clearly shown in the ozone figures quoted on page 339.

See paragraph on sp. gr. for relationship between sp. gr. and iodine value. Also see Williams (*J. Soc. Chem. Ind.*, 1900, **19**, 300).

For influence of atmospheric oxidation on constants see Sherman and Falk (*J. Amer. Chem. Soc.*, 1901, **23**, 156, 1905, **27**, 605).

Bromine Values.—McIlhiney[2] gives the following as being ordinary average figures for linseed oil:

Iodine value Hübl.	Bromine value	Bromine addition value	Bromine substitution value
170–185	105–115	100–110	less than 7

McIlhiney states that a low addition figure may be caused by rosin, rosin oil, benzene, or mineral oils, which usually have figures below 15, or by the presence of some other seed oil, *e. g.*, corn or cottonseed oil, which have figures of 73 and 63, respectively, or by boiled oil (old-fashioned boiling).

Turpentine is the only adulterant causing an addition figure higher than 110.

Bromine Substitution.—A higher figure than 7 indicates turpentine, rosin, rosin oil, benzene, or heavy petroleum. Mineral acid would also raise the figure, but this could be detected by high free acid value.

Insoluble Bromides.—Hehner and Mitchell, *Analyst*, 1898, **23**, 310, have made a number of experiments confirming those of Hazura and others as to the oxidation and bromination products of linseed and other drying oils. For details of these see p. 355.

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[1] *Chem. Zeit.*, 1898, **22**, 102. Also *Chem. Zeit.*, 1898, **22**, 558.

[2] Parker McIlhiney, Report on Linseed Oil to Commissioner of Agriculture, New York State, 1901, or see *J. Amer. Chem. Soc.*, 1899, **21**, 1084. *Et ibid.*, 1902, **24**, 1109.

Halphen (*J. Pharm. Chim.*, 1901, **14,** [8], 359) has modified Hehner and Mitchell's method, and applied same to the detection of drying and marine oils.

Lewkowitsch[1] has applied this test for the detection of raw linseed oils prepared at high temperatures. Lewkowitsch[2] prefers to brominate the mixed fatty acids (prepared with due precautions against oxidation).

In reference to hexabromides see Proctor and Bennett, *J. Soc. Chem. Ind.*, 1906, **25,** 798.

The test is of great value and importance in the examination of linseed oil for purity. See section on Adulteration.

Bromine Thermal Value.—See page 350 for values.

Combined Fatty Acids.—The m. p. of the linseed oil fatty acids has been found to vary from 17 to 24°, whilst the solidifying-point varies from 13.3 to 17.5°.

Lewkowitsch gives 19.0 to 19.4, 20.2 to 20.6 as the "titer" test of above.

Thoerner[3] states that there are 98% fatty acids present in the fat; sp. gr. at 100° = 0.9170; refractive index at 60° – 1.4546.

M. Tortelli and A. Pegami[4] have determined the molecular equivalent of insoluble fatty acids in linseed oil, and give the following table:

		Linseed oil, 3 years old	Linseed oil, fresh cold-drawn
Oil	acid value (1)	2.70	0.30
	saponification value (2)	192.1	189.8
Insoluble fatty acids	acid value (3)	191.5	194.6
	saponification value (4)	205.4	201.8
Mean molecular equivalent of fatty acids	calculated from acid value (5)	292.8	288.2
	calculated from saponification value (6)	273.2	277.9
Difference 5–6		19.6	10.3

The difference between the recorded and calculated molecular weights is ascribed by the authors to lactones. In order to avoid this error, they hydrate the lactones by boiling the fatty acids with an excess of alkali, and titrate the excess.

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[1] *Analyst*, 1904, **29,** 4.
[2] Chem. Tech. Fats and Oils, 1909.
[3] *Chem. Zeit.*, 1895, **18,** 1154.
[4] *Chem. Rev. Fett-Harz-Ind.*, 1902, **9,** 182, 204, 205.

Refractive Index.—Owing to the fact that the refractive index of linseed oil does not differ greatly from that of other oils, its value as a means of detection of adulterants is somewhat limited. Rosin, rosin oil, and mineral oil raise the refractive index, but it must be borne in mind that oxidation has the same effect. Weger[1] found (using a Zeiss refractometer) that a sample of raw linseed oil gave a reading of 80.2°, while, after treatment with 5% of manganese-lead resinate, this was raised to 85.8° and, after heating for 1 hour, to 86.7°.

Sjollema[2] prefers the refractive index to the iodine value as a means of detection of adulteration, and points out that the reading is lowered by the presence of fatty acids. Sjollema suggests a correction of 0.6 scale division for each degree centigrade when the temperature is not 15°, and confirms the fact that the refractive index is increased by oxidation.

Harvey,[3] as a result of the examination (using an Abbé refractometer) of 27 samples of linseed oil, obtained at 20° values varying from 1.4800 to 1.4812.

Proctor and Holmes,[4] using a Zeiss refractometer, found linseed oil with an iodine value of 174 had refractive index of 1.4825 at 15°; also linseed oil having iodine value 164 had refractive index 1.4817 (see "Blown Oils").

See also Thomson and Dunlop[5] whose values are quoted in paragraph on Iodine Values.

Polarimetric Rotation.—Linseed oil is (at any rate for all practical purposes) optically inactive, and therefore adulteration by rosin oil can be detected by its rotatory power.

Bishop,[6] using a Laurent saccharimeter—20 cm. tube—found −0.3° rotation by a sample of linseed oil.

Thoerner[7] found no rotation at 50−60°.

Filsinger[8] advises the use of a filtered solution of the oil in chloroform or alcohol, and gives the following figures as the result of the examination of four samples, two of known purity, and two commercial samples.

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[1] *Zeitsch. angew. Chem.*, 1899, 297.
[2] *J. Soc. Chem. Ind.*, 1903, **22**, 967. (Abstract.)
[3] *J. Soc. Chem. Ind.*, 1905, **24**, 718.
[4] *Ibid.*, 1905, **24**, 1289.
[5] *Analyst*, 1906, **31**, 283.
[6] *J. Soc. Chem. Ind.*, 1898, **17**, 990.
[7] *Chem. Zeit.*, 1894, (18), 1154.
[8] *Chem. Zeit.*, 1894, (18), 1005.

Samples of known purity		Commercial samples			
German seed oil for food	Indian oil for varnish	Dutch oil		English oil	
±0°	±0°	+28° (1)	+24° (2)	±0°	±0°

Filsinger used the polarisation apparatus of Schmidt and Häntsch—200 mm.—(as proposed by Aignan[1]).

Heat of Combustion.—Sherman and Snell[2] found the following heats of combustion.

Sample	Calories per gramme	
	Constant volume	Constant pressure
Linseed oil, 1900............	9364	9379
Linseed oil, 1898............	9379	9394
Linseed oil, several years old..	9215	9230
Boiled linseed oil............	8810	8824

The determination of the heat of combustion is of no value from an analytical standpoint.

Absorption of Ozone.—Fenaroli (*Gazetta*, 1906, **36,** [2], 292) has determined the ozone absorption of linseed oil (by the method of Molman and Soncini, *Ber.*, 1906, **39,** 2735). A sample of oil having an iodine value of 176.8 gave values of 33.4 and 34.6 for ozone, as compared with 33.5 calculated from the iodine value. He has also shown that the unsaturated fatty acids take up ozone exactly as required by theory.

Detection of Adulterants in Linseed Oil.

Linseed oil is liable to be adulterated in a variety of ways. The particular adulterant used is largely dependent on the prevailing prices of linseed oil and the adulterants. The likely adulterants are hydrocarbons, cottonseed oil (when cheaper), nigerseed oil, tung oil, fish oil; hemp-seed oil, rosin and rosin oil, rape oil, ravison oil, safflower oil, and candle nut oil.

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[1] *Compt. rend.*, 1890, **110,** 1273.
[2] *J. Amer. Chem. Soc.*, 1901, **23,** 164.

During the year 1909 the imports of Soya bean to England became considerable in quantity, over 400,000 tons being received. This has been crushed in quantity for the first time in England, and in view of the prevailing difference in the prices of Soya bean oil and linseed oil the adulteration of the latter by the former is not improbable and such adulteration must be sought for. The drying qualities of linseed oil would of course be impaired by such adulteration.

The following qualitative tests may be applied for the indication of adulterants, though their absolute reliablity cannot be vouched for. A quantitative examination is always advised.

Fish oils may often be detected by odour. The delicacy of this test is increased by rubbing the warm oil on the hands, and, according to Brannt, 0.01% of fish oil can be detected by this means. Fish oil adulteration can also be recognised by a peculiar scum which rises to the surface when such oils are boiled. Bearn blows steam through the warm oil and states that 2% of fish oil can be recognised by the fishy smell of the issuing steam.

The sulphuric acid colour test is a useful indication of the purity of linseed oil. With a genuine sample, a dark brown clot is formed; if rosin oil or fish oil be present, a reddish-brown spot quickly forms, which, in the former case, retains its red tint for a long time, while a peculiar scum forms over it. This test is also applicable to the detection of rosin oil in boiled linseed oil.

Fish oils may also be detected by the darkening produced by passing a rapid stream of chlorine through the oil or by the reddish colour produced by boiling the oil with alcoholic sodium hydroxide. As a test for cod oil, which is not unfrequently used in the case of linseed oil intended for the preparation of printing ink, A. Morell recommends the following test: 10 grm. of the oil are well agitated with 3 grm. of nitric acid, and the whole left to stand. With pure linseed oil the colour changes during the stirring to sea-green, afterward becoming dirty greenish-yellow, while the acid assumes a light yellow colour. In presence of 5% of cod oil, after standing some time, the oil is said to acquire a dark brown colour, and the acid is tinged orange or dark yellow, according to the proportion of the adulterant present. A similar test has been described by Conrath for the detection of rosin oil.

Japan wood oil is distinguished by the very hard black clot it gives with sulphuric acid, and by yielding a highly coloured semi-solid product with the Elaïdin test. If heated for a short time to about 300°, the oil becomes a transparent jelly, the change occurring either at once or on cooling.

Cottonseed can be detected by the Halphen colour reaction (see page 135). Rosin (colophony) can be detected by the Liebermann-Storch reaction. If the sample is very dark, Lewkowitsch recommends the extraction of the colophony with alcohol and the testing of this extract.

Lippert[1] is of opinion that the Liebermann-Storch reaction is not conclusive enough, but certainly ought not to be omitted in a qualitative examination.

The following statement shows how the different constants are affected by various adulterants, and will be of value in the examination of a suspected oil.

Effect of Adulteration on Characteristics of Linseed Oil.

Sp. Gr.—Mineral and foreign seed oils are lighter, while rosin and rosin oils are heavier; thus, by a judicious mixture of each class of adulterant, extensive adulteration can be effected without alteration of the sp. gr. A mixture of mineral and rosin oil may be used, rosin itself being sometimes also added. The mineral oil is usually of low sp. gr. (0.865–0.880) as the heavier oils are too greasy. The rosin oil employed for adulterating linseed oil is free from smell even when heated, but has a peculiar taste which is not masked by the linseed oil. Tung oil may be added as its sp. gr. is higher than that of linseed oil; it would, however, be detected by the bromide test.

Film Test.—By means of this test non-drying oils can be detected if present in sufficient quantity, the extent of drying varying with the extent of adulteration. Rosin oil causes linseed oil to remain "tacky" and prevents its ever becoming hard.

If the hydrocarbons are volatile, they may be removed by distillation in steam.

Solidification-point.—The solidifying point of pure linseed oil is given on page 70, and samples containing other seed oils solidify at a higher temperature. The same remark applies to the relative fusibility of the fatty acids, those prepared from cottonseed oil having an exceptionally high m. p.

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[1] *Chem. Rev. Fett-Harz-Ind.*, 1905, **12**, 4.

Maumené and Bromine Thermal Values.—The values obtained for linseed oil are not characteristic enough to be relied on as definite indications of adulteration, because some fish oils have both high iodine and thermal values.

Refractometer Reading.—By this means rosin and rosin oil and mineral oils may be detected.

Saponification Value.—Low saponification values may be due to adulteration by mineral oils, rosin oil, or turpentine. Rape oil is indicated by a low value. The small proportion usually present (by contamination in seed) is not detected.

Unsaponifiable Matter.—Adulteration by mineral oil and rosin oil will be detected by this estimation. Volatile hydrocarbons, such as benzene, turpentine, though unsaponifiable, will not be determined as such.

Iodine Value.—Lewkowitsch considers that if the iodine value of a linseed oil is below 170 it can be justly presumed that adulteration has taken place, either in the seed itself before the oil was expressed or in the oil, but insists on the recognition of the fact that a low iodine value is (under certain circumstances) quite consistent with purity. See paragraph on Iodine Value. A high iodine value is not in itself a proof of the purity, since fish oils, rosin oils, and even drying oils may be present in considerable quantities, and yet give figures quite within the range of ordinary practice. The tendency of foreign seed oils is to reduce the iodine value, while fish oils may scarcely have any effect at all. (See Thomson and Dunlop's figures in section on Iodine Values.) The phytosteryl acetate test is reliable for the detection of fish (liver) or blubber oils.

Bromine Values.—Turpentine will cause a sample of linseed oil to give high figures, while rosin and rosin oil will be indicated by a low bromine absorption and addition value, and a high bromine substitution value.

Insoluble Bromide Test.—This test is of great value in the detection of adulteration, as will be appreciated by an examination of the table given on page 355, where it is evident that many of the adulterants yield no insoluble bromides, or in any case much smaller quantities than pure linseed oil. The behaviour of insoluble bromides on heating is of importance. Fish oils which give high yields of insoluble bromides can be distinguished from linseed oil by their different behaviour on heating. The insoluble linolenic hexabromides from linseed oil melt definitely without decomposition at 175 to 180°, while the octobromides from fish (liver) or blubber oil become dark and decompose before melting at 200°. According to Lewkowitsch, it is possible to detect 10% of fish oil in linseed oil by such test.

Free Fatty Acids.—Rosin will cause a high figure, as also will mineral acids not properly washed out after refining. According to Lewkowitsch, linseed oil stock is frequently met with for soap-making and this contains much free fatty acid.

The amount of rosin can be estimated by titrating the oil with alkali, using phenolphthalein as indicator. Allowance must be made for the free acids usually present in linseed, and this seldom exceeds 3%. If linseed oil soap stock is to be examined, the rosin must be determined by Twitchell's method.

The report of the sub-committee on linseed oil of the American Society for Testing of Materials appointed by the Committee on the Preservative Coating of Iron and Steel fix the following specification for linseed oil during the year 1910. (From *Oil and Col. Jour.*, 1909, **36**.)

Raw linseed oil	Max.	Min.
Sp. gr. at 15°	0.836	0.932
Sp. gr. at 25°	0.931	0.927
Acid number	6.0	....
Saponification value	192	189
Unsaponifiable matter	1.5	....
Refractive index at 25°	1.4805	1.4790
Hanus iodine value	190	178

Drying of Linseed Oil.

Linseed oil is the most important of the class of drying oils. Its applications in the arts, as in the manufacture of paint, varnish, oilcloth, and printing ink, are all based on its drying properties. In consequence of its tendency to combine with oxygen, it evolves much heat when exposed to the air in a finely divided condition, sometimes sufficient to cause the inflammation of cotton-waste or similar material saturated with the oil.

According to Livache,[1] the property of absorbing oxygen and becoming converted into a tough or hard varnish is shared by all fatty oils of vegetable or animal origin. The transformation may be very slow, but it ultimately takes place. This tendency is much enhanced by heating the oil while passing a current of air through or over it (see "Boiled Oil"). By continued boiling the oil becomes very thick, and may be drawn out into elastic threads, which are very sticky but do not produce a greasy stain on paper. This product is used in the manufacture of printing ink. The drying of linseed oil is facilitated by the use of siccatives.

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[1] *Compt. Rend.*, 1895, (120,) 842.

When spread in a film, linseed oil dries to a substance known as linoxyn. Linoxyn is a neutral substance insoluble in ether or ordinary solvents. The constitution of linoxyn has not yet been ascertained, and it was formerly considered to be the final oxidation product of linseed oil. Reid,[1] however, has shown that on long exposure, from 2 to 5 years, depending on various conditions, it is transformed, first into a semi-fluid, and finally into a viscous fluid, which he terms "superoxidised linseed oil." The product is much darker in colour than ordinary linseed oil, is heavier than water, almost completely soluble in alcohol, soluble to a considerable extent in water, and strongly acid, forming solid compounds with most basic pigments. All drying oils yield linoxyn, the amount varying with the amount of linolenic or linoleic acid present. Lewkowitsch has proved that if linseed oil is kept protected from light, moisture, and air, it keeps indefinitely.

The chemical changes which occur in the boiling and drying of linseed oil are very imperfectly understood. According to Mulder, part of the linolin is decomposed during the boiling, with formation of linoleic anhydride, or a more highly oxidised body, such as hydroxylinoleic acid. According to Fox, the oxidation products are formed from the acids and the glycerol is decomposed into acids of the acrylic series, forming the irritating vapours which always accompany oil-boiling. Acetic and formic acids are prominent constituents of these vapours, and carbon dioxide and water are also present. The statements of Mulder and Fox are probably too sweeping. Allen isolated 8.8% of nearly pure glycerol from the products of the saponification of linseed oil which had been boiled by the steam process. Bauer and Hazura consider Mulder's explanation of the drying of linseed oil to be only partially correct. They investigated the subject and arrived at the following conclusions:

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[1] *J. Soc. Chem. Ind.*, 1894, **13**, 1020.

1. The more linolenic acid an oil contains, the more rapidly it dries.

Note.—It appears likely that the linolenic acids are the first attacked on drying and that linoleic acid plays a subordinate part, otherwise maize and cottonseed oils would have better drying properties.

2. The products of oxidation are not merely additive compounds, but contain part of their oxygen as hydroxyl groups. This is in conformity with the behaviour of unsaturated compounds in general. The oxidation of the salts is similar to that of the acids themselves.

3. By prolonged exposure to air at ordinary temperatures, or by shorter exposure at about 80°, the fatty acids are oxidised with formation of a resinous sticky solid, insoluble in ether, but reconverted into acids soluble in ether or heating with alkali.

4. The drying properties of oils depend upon the presence of linoleic, linolenic, and isolinolenic acids, as oleic acid forms no solid oxidation products. During the drying of linseed oil, only the glyceryl of the non-drying esters is oxidised, as is shown by the very small quantities of carbonic, formic, and acetic acids formed by passing pure air through pumice soaked in linseed oil. The samples of linseed oil which were still in the first stage of oxidation, as shown by their being still soluble in ether, contained 8.9 and 12.1% of free acid. The substance insoluble in ether, called by Mulder linoxyn, produced by the oxidation of linseed oil, is an ester termed hydroxylinolin. The drying properties of an oil appear to be in direct ratio to the proportion of the glycerides of linolenic and linoleic acids present.

The change of composition undergone by 100 grm. of linseed and poppy oils by exposure to air during 18 months was found by Clöez to be as follows:

	Linseed oil			Poppy oil		
	C	H	O	C	H	O
Composition of original oil..	77.57	11.33	11.10	77.50	11.40	11.10
Composition after 18 months.	72.27	10.57	24.16	71.38	10.64	25.08
Difference.	−5.30	−0.76	+13.06	−6.12	−0.76	+13.98

The quantity of oxygen absorbed was greater than that given off in the form of carbon dioxide and water, and the oil finally showed a considerable increase in weight.

Williams[1] gives the following table showing the change taking place in the elementary composition of linseed oil on boiling.

	1	2	3	4	5	6	7	8	9	10
C	75.03	75.40	74.66	74.32	67.74	69.52	64.74	65.40	68.64	64.35
H	10.78	10.64	10.38	10.04	9.57	9.49	9.01	9.00	9.24	9.01
O	14.19	13.96	14.96	15.64	20.69	20.99	26.25	25.60	22.12	26.61

Nos. 1 and 2, raw linseed oil; No. 3, moderately stout boiled oil; Nos. 4 to 10, solid oil, as used in manufacture of linoleum; No. 4, No. 5, Nos. 6 to 9, and No. 10, made by different processes.

According to Reid,[2] an increase in weight of 10% is observed in linoleum manufacture. This does not represent the actual gain in weight, as there is loss of volatile acids, carbon dioxide, etc. Toch[3] states that he obtained 19% oxygen absorption and that the quantity of carbon dioxide obtained never exceeded 0.8%.

Sabin[4] records results of experiments on the oxidation of linseed oil, in which it was found that air drawn through a series of flasks wetted with linseed oil dried the oil as follows: after a day or two the oil in the first flask began to bleach, and in due course dried, as was shown by the formation of a film of linoxyn, and then dried still further as indicated by the shrivelling and wrinkling of the film. During the whole of this time (about 10 days) the oil in the other flasks was not acted on. Then the oil in the second flask bleached and dried, then the third and so on. In 2 months, the whole series was dry. The removal of ozone from the air is suggested as an explanation of these results.

Shearman and Falk[5] have investigated the effect of atmospheric oxidation on the constants of linseed oil.

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[1] *Analyst*, 1898, **23**, 253.
[2] *J. Soc. Chem. Ind.*, 1898, **17**, 75.
[3] Toch. Chem. and Technology of Mixed Paints and Pigments, 1907.
[4] *J. Soc. Chem. Ind.*, 1906, **25**, 578.
[5] *J. Amer. Chem. Soc.*, 1903, **25**, 711.

	Fresh linseed oil	Exposed 8 months	Exposed till semi-solid
Sp. gr. at 15.5°	0.934	0.966	....
Hübl value	178.0	139.4	....
Maumené figure (Mitchell)	31.3°	32.8	....
Free acid as oleic	1.33	4.45	....
Reichert-Meissl number	0.49	2.64	....
C%	75.46	72.23	69.03
H%	10.92	10.46	10.06
o%	13.62	16.31	20.91
Ratio C:H	1.0:0.145	1.0÷0.143	1.0÷0.146

They state that the changes are less influenced by the sunlight than has formerly been supposed, and from further research the authors conclude that, in the case of non- and semi-drying oils, the iodine value of the original sample can be calculated from the sp. gr., or from the average figures for the kind of oil. With linseed oil this does not appear possible.

Effect of Driers.—The addition of driers during the boiling of linseed oil produces a product which dries more readily than raw oil. The part played by the drier in the boiling process was formerly considered to be that of a catalyst or oxygen carrier. Fahrion has, however, shown that when boiled oil dries some of the fatty acids are converted into oxidised acids. These oxidised acids are produced only to a very slight extent in the boiling of linseed oil, while Lewkowitsch has shown that polymerisation takes place during boiling. In view of the latest evidence, it must be considered that linseed oil on heating undergoes but very slight changes in its chemical composition. The addition of "driers" appears to result in the formation and solution of a metal salt of the fatty acids, which salts act as oxygen carriers, and thereby facilitate drying when the oil is exposed. Turpentine which is usually added to paints acts as an oxygen or ozone carrier and therefore assists drying.

Lippert,[1] Weger,[2] and Amsel[3] have studied the effect of various external influences on the drying of oils containing siccatives, and the reader is referred to their original papers for details.

Fokin[4] has studied the effect of a number of different substances on the oxidation of vegetable drying oils and has shown that the velocity of oxidation can be expressed mathematically.

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[1] *Zeitsch. angew. Chemie*, 1905 *et ante.*

[2] *Ibid.*, 1897 *et ante.*

[3] *Ibid.*, 1897 *et ante.*

[4] *Chem. Zentr.*, 1907, **2**, 1365, and *Zeitsch. angew. Chem.*, 1909, **22**, 1451.

It is of interest to note that the efficiency of a drier frequently decreases after a certain quantity has been added.

Influence of Light on Drying.—According to Clöez, the maximum amount of oxidation takes place with colourless glass, but with blue, red, green, or yellow, a longer time is required the nearer the colour approaches the yellow.

A. Genthe[1] has studied the effect of light on the process of drying, and has shown that:

1. Little or no oxidation takes place when flasks of brown glass are used and that the presence or absence of light greatly influences the rate of absorption of oxygen.

2. The full rate of absorption does not develop immediately. There is an induction period of about 2 hours, after which the absorption rate increases.

3. Using a "Uviol" lamp and vessels of "Uviol" glass, the same degree of oxidation was obtained in 1 day as required in parallel experiments 8 to 10 days in daylight and 50 days in dark.

4. The addition of siccatives caused no acceleration in the "Uviol" experiments.

5. Using resinates, oleates, and linoleates as siccatives the acceleration was 10 to 15% better in the case of the linoleates than the other two.

6. Violet rays apparently have the best drying effect.

7. That linseed oil first forms a primary catalyser and then acts as an accepter, and siccatives are to be regarded as pseudocatalysers, which have only a stimulative effect upon the formation of the primary auto-catalyser. This latter has not been isolated.

8. The results can be expressed by Ostwald's equation for autocatalysis. The amounts of oxygen absorbed by linseed oil in drying in the dark average 23% at ordinary temperatures, and 26.5% at 95°, while the amounts absorbed on exposure to Uviol light were 25.8% and 34.7%, respectively. The volatile products formed in the drying process are equal to 15% of the weight of oil.

The effect of light on the rate of drying of linseed oil is of technical importance, as also is the effect of different coloured rays on the colour of the dried film; especially is this the case when the oil is mixed with white lead. The writer is at present investigating the latter point.

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[1] *Zeitsch. angew. Chem.*, 1906., **19**, 2087.

This question was brought to his notice by the yellowing of white-lead painting which had dried in a room lighted only from a green-glass dome. The paint became yellowish after drying. Trial showed that the white colour of the paint was restored by exposure to sunlight. Petit states that white lead and linseed oil dried in the dark assumes a yellowish tint, while white lead and poppy oil do not behave in this manner. The writer has confirmed Petit's observation on linseed oil, but has invariably found that the yellow colour is removed by exposure to light; in fact, the change is reversible and appears to go on indefinitely.

Influence of Temperature.—Chevreul has shown that linseed oil dries more rapidly at 25°–28° than at 15°–18°.

Mitarewski[1] states that when oil is stored the temperature influences the degree of oxidation, and this is accelerated by storage at 70°. Exposure to light for 26 days had no effect.

Influence of Storage.—Fahrion considers that in oil which is kept the unsaturated acids polymerise, and that these complex bodies absorb oxygen rapidly. Chevreul has, however, found that short boiling yields a better drying oil than one which has been boiled for a longer period. It has been shown that polymerisation does not occur as suggested by Fahrion.

Relationship between Drying Properties and Iodine Values.—The iodine absorption of an oil stands in close relationship to the oxygen absorption, and consequently is indicative of the drying power. This relationship is clearly shown in paragraph on Ozone Absorption, better agreement being obtained than with oxygen values.

Fish and liver oils although having high iodine values do not dry like linseed oil and therefore the iodine value cannot be accepted as an absolute indication of drying power.

Characteristics of Linseed Oil.

Sp. gr.	0.931–0.937 at 15°
Solidification-point	−27°, stearine deposits at −25°
M. p.	−16 to −20°
Flash-point	450–500° F. (close), 258° open
Ash	from traces to 0.2% (limit)
Free fatty acids	0.5%–4%
Unsaponifiable matter	up to 2.0%, average 1.5%
Saponification value	183–221 mgrm. KOH, average 192

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[1] *J. Soc. Chem. Ind.*, (abstract), 1906, **25**, 818.

Reichert-Meissl value		0.50
Iodine value		175–190, sometimes higher
Bromine values	absorbed	105–115
	addition	100–110
	substitution	less than 7
Insoluble bromides		23–37%, average 25
Maumené test		90–145
Bromine thermal value		29.8–33
Refractive index		1.4800–1.4825 at 15°
Optical rotation		Practically nil.
Oleo refractometer		+48 to +54 "degrees"
Butyrometer		84–90′ at 20°
Viscosity		211.7, second at 70° F.

For characteristic constants of various varieties of seed, see works of Lewkowitsch, Wright and Mitchell, Benedikt and Ulzer, and other standard works; also Wijs, *loc. cit.;* Gill and Lamb, *Analyst*, 1900, **24**, 97; Thomson and Dunlop, *Analyst*, 1906, **31**, 281; P. McIlhiney, *loc. cit.*

Linseed Oil Fatty Acids.

Sp. gr.	at 15.0°	0.9158	Bearn.
	at 15.5°	0.9233	Allen.
	at 99° water at 15.5° = 1	0.8612	Allen.
	at 100° water at 100° = 1	0.8925	Archbutt.
Solidifying-point	13.3–17.5		Various.
	19.0–19.4 20.2–20.6	"Titer Test"	Lewkowitsch.
M. p.		24°	Allen.
		20–21°	De Negri and Fabris.
		17°	V. Hübl.
		Under 13°	Dieterich.
Insoluble fatty acids + unsaponifiable matter		= 95%	
Neutralisation value, mg. KOH		196–201	Various.
Mean molecular weight		283	Williams.
Iodine value		170–200	Various.
Acetyl value		8.5	Benedikt and Ulzer.
Refractive index		1.4546 at 60°	Thoerner.

Linoleic Acid.

Linoleic acid was isolated by Schüler in the following manner: Linseed oil was saponified with solution of sodium hydroxide, and the soap purified by repeatedly salting out. The aqueous solution of the soap was then precipitated by calcium chloride. From the well-washed precipitate the calcium linoleate was dissolved out by ether. The ethereal solution was decomposed by agitation with cold hydrochloric acid, the ethereal layer separated and distilled at as low a temperature as possible in a current of hydrogen. The residual acid had a dark-yellow colour, and was further purified by dissolving it in alcohol, saturating the solution with ammonia, and then precipitating with barium chloride. The barium linoleate thus obtained was washed, pressed, and repeatedly recrystallised from ether, and then converted into the acid by a treatment corresponding to that described for the calcium salt. The acid was dried in a vacuum over sulphuric acid and a mixture of ferrous sulphate and lime.

Reformatzky[1] claimed to have isolated the pure acid by the hydrolysis of pure ethyl linoleate, but this appears doubtful in view of the work of Hazura. It is probable that the substance prepared was a mixture of the unsaturated acids of linseed oil.

Linoleic acid is a thin oily liquid, of faint yellow colour. It remains liquid at —18°, and at 14° has a density of 0.9206. It is said to possess a faintly acid indication, and to have a taste which is at first pleasant and afterward harsh. Linoleic acid does not form a solid product on treatment with nitrous acid. With nitric acid it swells up considerably and yields suberic acid, $C_8H_{14}O_4$, a little oxalic acid, and a greasy resin.

Oxidation by potassium permanganate in the cold yields tetrahydroxy stearic acid. Linoleic acid dissolves readily in concentrated sulphuric acid, and in ether and alcohol.

On exposure to air linoleic acid absorbs oxygen, becoming thick and ultimately so viscid as scarcely to flow, but remains unchanged in colour. When spread in a thin layer on wood and exposed to the air, linoleic acid forms a varnish, but on glass only becomes tough. The product is said to have the composition of a hydrate of hydroxylinoleic acid, $C_{16}H_{26}O_3+H_2O$. When heated to 100°, this gives off 6.7% of water and becomes blood-red. By prolonged contact with air, and more quickly if frequently moistened with ether, colourless hydroxylinoleic acid loses its viscid consistence, and is converted into linoxyn.

Linoleic acid forms a tetrabromide the melting-point of which is stated to be 113–115°. Unlike linolenic acid, a hexabromide is not formed on treating with excess of bromine, though at an increased temperature 22% is converted into a higher bromide soluble in petroleum ether. Bedford[2] is of the opinion that two linoleic acids exist which differ in yielding a solid and a liquid bromo-derivative. The solid tetrabromide is soluble in ether, alcohol, benzene, chloroform, and glacial acetic acid, but only sparingly soluble in petroleum ether. On reduction by zinc and alcoholic hydrochloric acid it yields linoleic acid.

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[1] *J. Soc. Chem. Ind.*, 1890, **9**, 744.

[2] Inaugural Dissert., Halle a/S., 1906. Erdmann and Bedford, *Ber.*, 1909, **42**, 1324. Bedford and Rispe, *ibid.*, 1334.

Linoleates.—The salts of linoleic acid are difficult to obtain pure. They are white, amorphous (except in the case of the zinc salt), bodies which become coloured on exposure to air, and are soluble in alcohol and ether. Potassium and sodium linolates containing an excess of alkali absorb oxygen rapidly and become yellow and dry when exposed in a finely divided state to the air, dissolve in water with dark brownish-red colour, and give, on addition of hydrochloric acid, a brown greasy resin. The ethereal solution of lead linoleate, when evaporated on a glass plate, leaves a white amorphous residue of lead hydroxylinoleate. The acid separated from this salt by hydrogen sulphide and dissolved in alcohol remains on evaporation as a nearly colourless viscid mass, which becomes blood-red without change of composition when heated to 100° or treated with acids or alkalies. The colourless alcoholic solution of hydroxylinoleic acid is not altered by alkali carbonates at the boiling heat, but caustic alkalies turn it red even at ordinary temperatures.

Linolenic Acid.

Linolenic acid has been prepared by reduction of its hexabromide obtained from linseed oil.

The acid is a nearly colourless oil having a sp. gr. at 15.5° of 0.9228.[1] Linolenic acid rapidly absorbs oxygen on exposure to the air, becoming brown in colour. The hexabromide melts at 179°–181°.

Bedford (*loc. cit.*) is of the opinion that two isomerides of linolenic acid exist, one which yields a solid hexabromide, melting at 179°–180°, the other a liquid tetrabromide. The existence of isolinolenic acid is debatable, its existence as a glyceride has been suggested by Hazura, but Bedford considers that the liquid tetrabromide of linolenic acid has been mistaken by Hazura for the soluble isolinolenic hexabromide.

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[1] Hehner and Mitchell, *Analyst.*, 1898, **23**, 313.

Miscellaneous Notes.

Linseed oil has the property of dissolving sulphur, and at 77° F. dissolves 0.630%; at 320° F. 9.129%. On cooling the solutions, sulphur is deposited slowly.

The official *Balsamum sulphuris* is prepared by boiling linseed oil with 0.25% of sulphur. A dark viscous mass is obtained.

The absorption of phosphorus by linseed oil has been investigated by Katz.

Nitrous acid does not give a solid elaïdin with linseed oil.

Nitric acid interacts with linseed oil—the rate depending on the strength of acid employed. A moderately strong acid converts linseed oil into a viscid mass insoluble in petroleum ether, while fuming nitric acid inflames it. For method of detection of linseed oil in walnut oil, see Halphen, *Bull. Soc. Chem.*, [6], 1905, **33**, 571.

BOILED LINSEED OIL.

When linseed oil is heated, its drying properties are considerably increased if, during the heating, certain substances known as "driers" are present.

The earliest process consisted in heating the oil by fire in a boiler to a temperature of 210 to 260° in the presence of driers. This process has been almost entirely superseded by newer processes, which have the merit of yielding products paler in colour and requiring a lower temperature for their application. Among these processes may be mentioned that of heating the oil to about 150°, in a steam-jacketed, agitated vessel, whilst in some cases air is blown through. In the Hartley-Blenkinsop process a still lower temperature is employed (120°) by using a soluble drier (manganese linoleate).

According to various writers, it is a somewhat common practice to add soluble driers to unboiled linseed oil, and to sell the mixture as "boiled oil," which is known in the trade as "bung oil." Such oil has exactly the same constants as unboiled oil, but does not dry so well as oil which has been boiled. Among painters and others using boiled oil there is considerable doubt frequently expressed as to whether oils made by the newer processes are as good as those produced when only lead driers were used in the boiling. Boiling increases the sp. gr. and viscosity of linseed oil, the extent of each increase being dependent on the extent of boiling and method used. Fire boiling is said to produce the most viscid product.

The colour of boiled oil varies according to the method and time of manufacture, and also the original colour of the oil used. It is a common practice among oil refiners to use their dark oil for boiling purposes. Boiled oil is of a darker colour than raw oil, and is of a reddish-brown shade. Lead driers are said to produce a dark coloured oil.

Boiled oil can be distinguished from unboiled by the presence of a metallic residue (due to driers) when ignited, and also by following characteristics.

Sp. Gr.—0.932–0.945; according to McIlhiney, the sp. gr. may be as high as 0.950, but is seldom over 0.940.

Iodine Value.—Williams gives the following table showing the decrease in the iodine value which takes place on boiling.

	Thin	Thin	Stout	Very stout
Iodine value,	111.3	112.4	65.6	59.9

The above figures are probably too high, as the Hübl solution was allowed to act for 18 to 20 hours. See section on Drying of Linseed for changes in ultimate composition which take place on boiling.

Lewkowitsch has shown that it is necessary to remove the metal from a boiled oil by treatment with mineral acids before determining the iodine value, otherwise the value obtained will be too high.

McIlhiney[1] has modified his process for the estimation of bromine absorption in the case of boiled oil and linseed oil in presence of driers. (See original paper.)

The nature of the driers added to linseed oil can be generally inferred from an examination of the ash left on burning a quantity of the sample, a little at a time, in a porcelain dish. The residue should be specially tested for lead, copper, zinc, iron, manganese, and borates. Sulphates, acetates, borates and other salts may be detected by agitating the original oil with a solution of sodium carbonate, separating the aqueous portion, and examining the solution in the usual way, or by boiling 25 grm. of the sample with dilute hydrochloric acid for half an hour with constant stirring, allowing to separate into 2 layers, and syphoning off the acid layer, and testing by ordinary methods for metals (lead, manganese) and acids (boric, oxalic, etc.).

M. Kitt (*Chem. Rev. Fett-Harz-Ind.*, 1901, **8**, (3) 40) gives the following table, showing the alterations taking place on boiling linseed oil. The numbers (from 0 to 6) represent the different stages from thin oil to the consistency of india rubber.

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[1] *J. Amer. Chem. Soc.*, 1902, (24), (11), 1109.

No.	Acid value	Saponification value	Iodine value	Iodine value of fatty acids	Acetyl acid value	Acetyl saponification value
0	4.8	188.9 188.6	159.3 158.6	158	153.5	178
1	5.2	189.9 188.3	101.4 100.1	107.3	191.3	201.7
2	7.8	189.1	95.6	100.1	192.4	208.0
3	9.5	186.6	83.6	88.1	188.2	206.2
4	9.1	187.2	79.1	85.6	....	....
5	11.7	187.2	76.2	81.9	193.4 192.6	213.1
6	18.8	192.3	71.1	....	....	210.9

Insoluble Bromides.—According to Lewkowitsch,[1] the best test for the detection of raw linseed oils in boiled oils prepared at an elevated temperature is the hexabromide test.

Oils heated to a high temperature undergo polymerisation and give decreased yields of hexabromides. The yield of hexabromide rapidly decreases as the temperature used for the preparation of the oil is increased. The following table by Lewkowitsch bears out the above statements. Figures are also given showing the effect of ozonisation of linseed oil. In this case the treatment was carried out at a temperature below that at which polymerisation takes place, hence the yield of hexabromides and the iodine value are little altered from that of the original sample.

Name	Sp. gr.	Iodine value	Hexabromides from glycerides
Linseed oil—raw	0.9308	186.4	24.17
Pale boiled linseed	0.9429	171.0	20.97
Double	0.9449	169.96	13.03
Ozonised	0.9310	180.1	36.26–36.34
Ozonised	0.9388	171.2	25.73
Ozonised	0.9483	169.7	30.19
Safflower oil—raw			
Double boiled safflower	0.9266	146.46	traces
Pale	0.9360	137.3	....
Pale	0.9361	139.1	....
Double	0.9447	137.0	....
Double	0.9503	141.8	none
		127.3	

Unsaponifiable Matter.—There is no appreciable increase in the unsaponifiable matter on boiling. See paragraph on unsaponifiable matter in linseed oil.

Drying.—The rate of drying of boiled oil is important, and it must be again pointed out that in order to obtain figures of any value, great care must be taken to obtain exactly similar conditions during comparative trials. See section on Drying of Linseed Oil.

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[1] *Analyst*, 1904, **29**, 2.

The United States Navy Department Specification, 1905, demands that boiled linseed oil must be pure kettle-boiled oil, free from rosin. A film left after flowing the oil over glass and allowing to drain in a vertical position for 12 hours, must be dry, free from tackiness in 12 hours at a temperature of 70° F.

For the rules of testing boiled linseed oil issued by the Russian Minister of Marine, see *J. Soc. Chem. Ind.* (abstract), 1905, **24,** 155.

Uses.—Boiled oil on drying gives a somewhat hard film, which is liable to crack on exposure, and it is therefore the custom, in painting, to add a little raw oil in order to give a more elastic and durable coat. The detection of small quantities of raw linseed oil in boiled oil is therefore of little or no importance.

Adulteration.—Boiled oil is adulterated in the same manner as linseed oil (see paragraph on Adulteration), and adulteration is more frequent in the boiled variety. The usual adulterants are rosin, mineral and rosin oils, tung and fish or blubber oils.

A large number of substitutes are marketed and they are usually compounded from the above.

It must be pointed out that boiled oil containing liquid driers may legitimately contain a small proportion of turpentine.

The following test is frequently recommended as a rapid method of detection of adulteration. Add water after saponification with alcoholic potassium hydroxide: if a strong turbidity is produced it indicates the presence of adulterants. This test has, however, been investigated by Lippert[1] who has proved it to be unreliable. Lippert[2] states that linseed oils boiled with lead or manganese oxides give only brown colourations with Storch-Morawski's test, while red or blue colourations are obtained when rosinates, rosin, or fish oils are present. Maize oil gives similar reactions.

Lithographic Varnishes.—If the temperature of heating of linseed oil be raised to 250 to 300°, the so-called lithographic varnish is obtained. The time of boiling determines the viscosity of the product. Driers are not used in the preparation of lithographic varnishes. Lewkowitsch has shown that the process taking place is one of polymerisation, and states that oil prepared by blowing is not suitable for varnish manufacture. For further details *re* varnishes, see Leeds, *J. Soc. Chem. Ind.*, 1894, **13**, 203, and Lewkowitsch, Chem. Technology of Oils and Fats, 1909.

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[1] *Zeitsch. angew. Chem.*, 1897, 655.
[2] *Chem. Rev. Fett-Harz-Ind.*, 1905, **12,** 4.

	Sp. gr. at 15°	Acid value (oleic)	Unsaponifiable matter %	Sap. value	Iodine value
Very thin stand oil........	0.9452	3.19	0.35	186.5	157
Thin stand oil............	0.9465	4.43	0.27	178.4	123.2
Medium stand oil.........	0.9574	5.25	0.31	183.8	115.4
Stout stand oil...........	0.9589	6.90	0.38	182.0	75.1
Very stout stand oil........	0.9676	10.20	0.43	190.3	59.0

The above figures for stand oils are an average of a large number of results on different batches, each batch being heated to 300° and fired, the time of heat varying according to the thickness of the litho-varnish required. (Bearn.)

Differentiation between Boiled and Unboiled Linseed Oil.—In addition to the previous tests described, the following must be mentioned:

Finkener recommends the following test as being rapid and suitable for Customs House work, claiming that 25% of boiled oil can be detected. 100 grm. cryst. lead acetate and 32 grm. of glycerol are dissolved in 150 c.c. of water; 5 c.c. of this solution are mixed with 1 c.c. of 20% ammonia, this solution is added to 12 c.c. of the sample, the mixture shaken actively, and then heated to 100° for 3 minutes.

If the sample is pure linseed oil, it will form two layers on standing, the lower one being clear, while if the sample contains boiled oil, it will set to a soft viscous mass.

Evers,[1] examined the test, and found that it holds good for oils boiled with driers, but oil prepared by merely boiling down to a certain volume while air is blown through) behaves like raw linseed oil. The test is therefore merely for the presence of driers.

Evers recommends the following test of Morpurgo[2] who distinguishes by saponifying the oil and dissolving the soap in water. The resulting clear solution is treated with common salt until no more soap separates out. If after filtration the filtrate is made strongly acid with acetic acid, a turbidity shows that the oil used was boiled, while if it remains clear, the oil was raw.

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[1] *Chem. Zeit.*, 1899, **23**, 334.

[2] *J. Soc. Chem. Ind.*, (abstract), 1897, **16**, 470.

A very useful test to distinguish between raw and pale boiled oil is to shake the sample with ammonium sulphide when a dark colouration is obtained (Bearn).

The analysis of a sample of boiled linseed oil, which, in addition to containing various mineral additions and free fatty acids, is also adulterated with rosin, rosin oil, and mineral oil, is a complex problem. The following plan is recommended: The substantial accuracy of the results has been established by Allen: 25 grm. of the sample should be shaken in a separator several times with dilute hydrochloric acid. The aqueous liquid, which may contain lead, zinc, manganese, borates, and other mineral additions, is separated from the oily layer, and the latter is washed by agitation with water till the washings no longer redden litmus. The oil is then treated with rectified spirit, and the free fatty and resin acids titrated with standard alkali and phenolphthaleïn. The neutral point having been reached, the alcoholic layer is separated from the residual oil, which consists of neutral fatty oil and hydrocarbon oils of the original sample. These may be separated in the usual manner. The alcoholic solution is then concentrated, water added, and any globules of oil dissolved by agitating with petroleum spirit. After separation from the aqueous liquid, and evaporation of the solvent, the small residue of neutral oils may be weighed, and the amount found added to the main portion. The aqueous solution is then acidified with dilute hydrochloric or sulphuric acid, when an oily layer is obtained, consisting of the free fatty and rosin acids of the original sample, together with such additional amount as may have been formed by the decomposition of metallic soaps in the first stage of the process. This is separated from the aqueous liquid, washed with a little water, and filtered through wet paper. On subsequently drying the filter in the water-oven, the fatty acids pass through, and can be collected in a small tared beaker, the portion remaining on the filter being dissolved in ether. After weighing the fatty acids in the beaker, 1 grm. is treated by Twitchell's process for the separation of fatty and rosin acids. The amount of rosin thus found, subtracted from the mixed fatty and resin acids, gives that of the fatty acids alone. By agitating the original sample with alcohol, separating the solution from the undissolved oil, and titrating the former with standard alkali, the sum of the fatty and rosin acids originally existing in the oil can be ascertained.

Driers.—Among the siccatives formerly in use were litharge, ferric oxide and manganese dioxide. These solid siccatives have been almost entirely replaced by soluble compounds. The latter possess the advantage that they may be incorporated with the oil at a lower temperature or even in the cold if the siccative has been previously dissolved in turpentine. Compounds containing lead only are but little used, the ordinary preparations being manganese rosinate, lead and manganese rosinate, manganese linoleate, and lead and manganese linoleate (*i. e.*, preparations obtained from the mixed linseed oil acids). Products obtained with other metals, such as copper and zinc, have been found to be useless. The rosinates are made either by melting together with rosin, usually colophony, with the metallic oxide, or by saponification of the rosin and precipitation from the aqueous solution of the soap by means of a salt of manganese or lead.

To be effective the siccative should be completely soluble, any suspended oxide being not only valueless but harmful. The solvents employed in testing the preparation are ether and (in the case of lead rosinate) chloroform. When insoluble in these, the sample will be insoluble also in moderately hot linseed oil, and therefore worthless. (Lippert, *Zeits. angew. Chem.*, 1903, 366.)

From the examination of a large number of samples Weger (*Zeits. angew. Chem.*, 1896, 531) finds that the soluble manganese in fused rosinates seldom exceeds 2.3%, but in precipitated rosinates it may reach 6% or even 7%. Good preparations of fused manganese linoleate have 9% and in some cases even 11%. The preparation most used is fused lead and manganese rosinate; the most suitable proportion of lead to manganese appears to be 5 to 1. For the analytical examination, Weger burns off the organic matter and estimates the manganese and lead in the ash. It is useless to weigh the total ash, as rosinates often contain sand. If, after the removal of the lead, calcium is present to any extent, the manganese and calcium are estimated together in neutral solution as carbonates, the manganese titrated and the calcium estimated by difference. The insoluble lead and manganese are estimated by dissolving a fresh portion of the siccative in ether or chloroform, filtering, washing, igniting, etc. The soluble manganese is estimated by the difference between this result and that of the total manganese, and the result may be controlled by estimating the soluble manganese in an aliquot portion of the filtrate. The soluble lead must be ascertained by difference, since the chloroform cannot be completely evaporated from the rosinate solution, traces remaining except at a red heat, when most of the lead volatilises with it as lead chloride.

The analytical examination of a drier is in itself of little value as an indication of its properties.

Patent driers under fancy names are frequently met with. The number of such materials is legion, and many are worthless products containing large quantities of inert substances which have no siccative properties and merely act as diluents.

References to Literature Relating to Driers.

Thorpe. *J. Soc. Chem. Ind.*, 1890, **9,** 628.
Hartley. *J. Chem. Soc.*, 1893, 63, 129.
Weger. *Zeits. ang. Chem.*, 1896, 531.
Weger. *Ibid.*, 1897, 401, 542, 560.
Lippert. *Zeitsch. angew. Chem.*, 1900, 133.
Lippert. *Chem. Zeit.*, 1903, **16,** 365.
Fawsitt. *J. Soc. Chem. Ind.*, 1903, **22,** 538.
Endemann and Paisley. *Amer. Chem. Jour.*, 1903, **29,** 68.
Lippert. *Zeit. f. angew. Chem.*, 1905, 94.
Täuber. *Chem. Zeit.*, 1906, 1252.
Meister. *Färber-Zeit.*, 1908, 153.
Lewkowitsch. *Loc. cit.*, **3,** 106.
Fokin. *J. Soc. Chem. Ind.*, 1907, **26,** 1149.

When a drying oil containing manganese oxide in solution is dissolved in an equal volume of benzene and agitated with air in a closed vessel, rapid absorption of oxygen takes place, especially at a temperature of 40 to 50°. If the supply of air is repeatedly renewed, the liquid becomes thick, and on distilling off the solvent a residue is obtained which solidifies on cooling to a dry and perfectly elastic solid. By limiting the oxidation, various intermediate products are obtainable. The last product is characterised by its elasticity and its insolubility in water, alcohol, and ether. It is almost instantly saponified by sodium hydroxide in the cold; and on subsequent separation of the fatty acids, it is found that the solid acids have undergone no alteration, while the liquid fatty acid has been converted into viscous products, characterised by their solubility in water and by the salts which they form.

For later investigation of above, see Dunlap and Shenk, *J. Amer. Chem. Soc.*, 1903, **25,** 8, 826.

BLOWN OILS, OXIDISED OILS, BASE OILS, OR "SOLUBLE CASTOR OILS."

Various products known by these or similar names are manufactured by blowing a stream of air through fatty oils. The oils which lend themselves most readily to the treatment are cotton, rape, and linseed oils, but the process is also carried out with olive, lard, ground-nut, and some fish oils, the latter being almost entirely used in the leather industries.

Cottonseed, rape, and linseed oils are the most usual oils used. Blown cottonseed oil and rape oil are respectively known as lardine and rapine. The oil is usually heated by a steam coil at the commencement of the blowing to a temperature of 70°, though this is not strictly necessary, at least with certain oils: care must be exercised to avoid too high a temperature (above 80°), except in certain cases in which a temperature of 110 to 115° is employed. The process usually lasts from 12 to 48 hours, according to the nature of the oil under treatment, the character of the product desired, and the size and power of the apparatus. A considerable rise in temperature takes place, and provision has to be made to prevent this becoming too great. The quality of the product can be varied by arresting the process at any particular stage.

The blown oil is usually of a clear yellow colour, with a disagreeable smell and taste suggesting its origin.

The temperature of working has some influence on the rate of oxidation, the action being hastened by high temperatures; the products obtained from high temperature oxidation are usually darker in colour and have a more pronounced odour that those prepared at lower temperature.

The perfect miscibility of such oils with heavy mineral oils gives them an advantage over castor oil in the manufacture of lubricating mixtures for heavy machinery, hence the term "soluble castor oil." Opinions are divided as to the suitability of blown oils as lubricants. They are stated to be useful on account of their high sp. gr. and viscosity. Some authorities, however, look on them with suspicion, as they object to the low flash-point, and the liability of such oils to "gum."

Mineral and castor oils are mutually soluble only to a very limited extent, but by addition of some other oil, such as tallow oil, perfect union can be obtained. When the oxidation of cottonseed oil is pushed to an extreme, the product has a sp. gr. of 0.885, and is not readily miscible with heavy mineral oils. Blown oils yield sebacic acid on dry distillation, and contain but an insignificant proportion of unsaponifiable matter. The odour, taste, and colour-reaction of the oil with sulphuric acid will afford an indication of its origin, and more definite information can be obtained by an examination of the physical and chemical characters of the fatty acids produced by its saponification.

Oils, on being blown, increase in viscosity, and in the case of linseed oil the oxidation is continued until the oil has become solid for linoleum-making. The solidified oil obtained is heavier than water.

References for linoleum: Pinette, *Chem. Zeit.*, 1896, **16,** 281; Reid, *J. Soc. Chem. Ind.*, 1896, **15,** 75; Lewkowitsch, *Analyst*, 1902, **27,** 140; Ingle, *J. Soc. Chem. Ind.*, 1904, **23,** 1197.

Leeds[1] gives the results of the examination of two oxidised linseed oils prepared by blowing linseed oil with oxygen in a jacketed pan.

The oxidised oils are more readily soluble in alcohol than the original oils. Benedikt and Ulzer[2] give the following table as showing the solubility of 1 part of blown oil in alcohol.

Cottonseed oil dissolved in 35.7
Blown cottonseed oil (laboratory sample), 22.9
Blown cottonseed oil (commercial sample), 14.9
} parts absolute alcohol at 18°.

Fox and Baynes,[3] Thomson and Ballantyne,[4] Chapman and Rolfe,[5] have examined a number of blown oils.

Fox (*Oil and Col. Journ.*, 1887, **8,** 549) has published the following figures, showing the changes produced in oils by blowing with air:

	Linseed		Cottonseed		Rapeseed	
	Before	After	Before	After	Before	After
Sp. gr.	0.9354	0.986	0.916	0.9685	0.927	0.985
Glycerol	9.36	12.85	9.64	11.32	9.61	11.68
Free fatty acids	2.40	2.73	2.50	3.70	3.20	5.35
Insol. fatty acids	95.70	87.67	95.43	84.70	95.65	85.50

At a more recent date, Lewkowitsch has made a thorough investigation into the blowing of oils, and tables A, B, C, and D are extracted from his paper in the *Analyst*, 1902, **27,** 683.

[1] *J. Soc. Chem. Ind.*, 1890, **9,** 847.
[2] *Zeitsch. angew. Chem.*, 1887, 245.
[3] *Analyst*, 1887, **12,** 33.
[4] *J. Soc. Chem. Ind.*, 1892, **11,** 506.
[5] *Chemical News*, 1894, (701), 2.

CHARACTERISTICS OF BLOWN OILS. Lewkowitsch.

TABLE A.

Blown oil	Neutralisation value	Saponification value	II–I	Iodine value	Total soluble acids	Sp. gr.	Unsaponifiable matter	Oxidised acids	Hehner value	Acetyl value		Saponification value after acetylation	Hehner value after acetylation	XII–II
										Apparent	True			
No.	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
	Mg. KOH	Mg. KOH	Mg. KOH	%	Mg. KOH		%	%		Mg. KOH	Mg. KOH	Mg. KOH		
Ravison rape...	10.47	198.31	187.84	72.66	36.89	0.9685	1.23	21.22	83.52	88.37	52.93	243.2	....	44.9
East India rape.	13.25	215.57	202.32	61.92	56.26	0.9623	0.93	20.74	82.18	102.87	46.61	253.33	....	37.76
Cotton seed	9.41	224.59	215.18	65.74	46.49	0.9785	1.37	29.39	82.59	110.73	64.29	273.30	83.85	48.71
Maize	7.33	208.63	201.30	90.7	49.13	0.9806	2.28	31.93	82.34	113.16	63.37	268.75	....	60.1

CHARACTERISTICS OF MIXED FATTY ACIDS. Lewkowitsch.

TABLE B.

Mixed fatty acids from ..	Neutralisation value	Saponification value	II–I	Iodine value	Total soluble acids	Hehner value	Acetyl value		Saponification value of acetylated acids	IX–II	Hehner value of acetylated acids
							Apparent	True			
No.	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
	Mg. KOH	Mg. KOH		%	Mg. KOH		Mg. KOH	Mg. KOH	Mg. KOH		%
Blown ravison rape oil...	175.14	191.7	16.56	73.31	7.26	....	50.0	42.75	227.4	35.7	....
Blown East India rape oil	171.93	190.0	18.07	60.80	10.71	....	66.2	55.5	237.8	47.8	....
Blown cottonseed oil ...	194.79	210.46	15.67	72.43	12.94	93.76	67.35	55.67	254.8	44.4	92.11
Blown maize oil	192.8	209.93	17.13	88.08	29.45	86.4	88.97	59.52	267.3	57.37	....

CHARACTERISTICS OF OXIDISED ACIDS. Lewkowitsch.

TABLE C.

Oxidised acids from	Neutralisation value	Saponification value	II–I	Iodine value	Total soluble acids	Hehner value	Acetyl value		Saponification value of acetylated acids	IX–II	Hehner value of acetylated acids.
							Apparent	True			
No.	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
	Mg. KOH	Mg. KOH		%	Mg. KOH		Mg. KOH	Mg. KOH	Mg. KOH		
Blown ravison rape oil...	171.5	208.0	36.5	49.14	22.56	....	102.5	80.0	307.5	99.5	....
Blown East India rape oil	173.3	211.3	38.0	39.79	22.35	....	128.0	105.65	315.9	104.6	....
Blown cottonseed oil....	174.7	220.71	46.01	48.6	36.12	....	154.4	118.28	322.69	101.98	83.85
Blown maize oil	171.94	215.74	43.60	70.87	48.0	95.53	173.58	126.68	326.45	111.11	....

CHARACTERISTICS OF FATTY ACIDS FREED FROM OXIDISED ACIDS. Lewkowitsch.

TABLE D.

Fatty acids freed from oxidised acids from	Neutralisation value	Saponification value	II–I	Iodine value	Total soluble acids	Hehner value	Soluble acids	Acetyl value		Saponification value of acetylated acids	X–II	Hehner value of acetylated acids
								Apparent	True			
No.	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
	Mg. KOH	Mg. KOH	Mg. KOH	%	Mg. KOH	%	Mg. KOH	Mg. KOH	Mg. KOH	Mg. KOH		
Blown ravison rape oil...	176.8	188.6	11.8	61.88	6.97	....	6.75	42.5	35.53	220.3	31.7	....
Blown East India rape oil	166.6	176.8	10.2	55.93	10.09	....	8.85	47.13	37.54	219.2	42.95	....
Blown cottonseed oil	188.0	196.15	8.15	56.02	11.0	....	7.27	33.69	22.69	232.0	33.6	96.17
Blown maize oil	172.37	177.68	5.31	85.52	6.14	85.54	7.54	43.8	36.7	228.76	50.52	....

The investigations show that blowing results in the following changes: The sp. gr. is increased and the free acid and saponification values are also increased. The saponification values of the oxidised acids are higher than the neutralisation value, thus pointing to the presence of lactones. Saponification of the blown oil is more difficult than that of the original oil. Soluble acids are formed, hence the Hehner value is low. The iodine values decrease, and the oils acquire a considerable acetyl value. The oxidised acids are insoluble in petroleum ether, but separation by this solvent is not complete. There does not appear to be any numerical connection between the acetyl value and the oxidised acids.

Lewkowitsch also gives the following table as the result of heating linseed and cottonseed oil to 120°, while air was blown through.

TABLE SHOWING CHANGES IN BLOWING OF LINSEED AND COTTONSEED OILS.

Lewkowitsch.

Oil blown at 120°.

	Orig. oil		After 2 hrs.		After 4 hrs.		After 6 hrs.		After 10 hrs.	
	L	C	L	C	L	C	L	C	L	C
Oxidised oil										
Sp. gr. (1) at 15.5°	......	0.9250	0.9334	0.9262	0.9403	0.9291	0.9446	0.9350	0.9460	0.9346
Saponification value (2)	......	......	189.8	194.3	191.3	194.9	192.4	196.1	192.7	196.8
Total volatile fatty acids in terms of (3) milligrams KOH	0.8	0.1	1.68	2.88	3.0	2.44	8.3	4.60	0.9	4.16
Oxidised acids (4), %	......	......	1.2	0.51	1.7	0.87	5.03	0.94	7.1	1.28
Acetylated oil										
Saponification value (5)	205.6	200.21	200.9	203.9	203.9	212.0	208.2	215.2	211.8	218.4
Hehner value (6)	96.2	95.7	94.4	94.8	94.6	92.9	93.2	91.9	92.1	91.4
Apparent acetyl value (7)	12.5	7.7	18.9	14.2	22.5	22.9	25.5	30.0	32.6	35.0
True acetyl value (8)	11.7	7.6	17.22	11.32	19.5	20.46	17.2	25.4	31.7	30.84
Difference 5–2	......	......	11.1	9.6	12.6	17.1	15.8	19.1	19.1	21.6

Proctor and Holmes have investigated the process of the oxidation of oils by blowing. The method adopted was that of blowing air through 100 c.c. of oil contained in a test-tube, which was heated to 100° by means of a water-bath. At intervals samples were drawn, and the refractive index and iodine value determined. The following are the most important results and conclusions:

Without exception, on blowing any oil, the sp. gr. and refractive index increase as oxygen is absorbed, and at the same time the iodine value, which is a measure of unsaturated linkages, diminishes as these become saturated with oxygen. In no case, however, was it found that in 24 hours' blowing the oil at all approached complete saturation, and even in commercial blown and oxidised oils the iodine value shows that saturation is far from complete.

The process of oxidation is a somewhat complicated one. An interesting peculiarity which is striking in several oils (especially Moellers codliver and pale seal) is that the iodine value remains practically unaffected during the first three or four hours of blowing, though the rise of sp. gr. and refractive index shows that oxygen is being absorbed. This, of course, indicates that the saturated linkages which are measured by the iodine absorption are still unopened, and that oxygen is temporarily retained merely in solution or in some other way than direct linking on the carbon chain. Usually, when a drop in the iodine value does set in, it proceeds rapidly for some time, as if the oxygen previously absorbed now took its place in the broken linkage. In other cases, as in castor oil, little or no change takes place in any of the constants during the first three hours of blowing, while in the second three it is relatively rapid.

Polymerisation does unquestionably take place, affecting the refraction and sp. gr., but probably not affecting the iodine value or perhaps the refractive constant, in which the natural relation between refractive power and density is taken into account.

The following table gives the figures before and after the experiments. For intermediate values, see original paper. (*J. Soc. Chem. Ind.*, 1905, **24**, 1287.)

The only oil in which the dispersion is probably high is whale oil, and constants are given in a table, of which the original dispersion was 44.5, rising on blowing to 47.5, the other constants being quite normal. The refractive indices and dispersions of three other whale oils given in Table XX of paper are very constant, beginning at 39.9 to 40.0 and ending in all cases at 40.8, so that it is evident that high dispersion is not a usual characteristic.

Note.—All oils were blown at 100°, and measurements taken at 15°. Iodine values by Hanus method. Refractive index measured by a Zeiss refractometer.

Oil	Sp. gr.	Refract. index	Ref. const.	Disp.	Iodine value
Skate liver oil	0.926	1.4830	0.3084	39.6	187.0
Blown 24 hours	0.937	1.4843	0.3055	39.8	159.0
Möellers' codliver oil	0.924	1.4814	0.3082	39.5	163.0
Blown 24 hours	0.969	1.4848	0.2957	40.1	117.0
Codliver oil	0.930	1.4812	0.3061	39.7	156.0
Blown 18 hours	0.943	1.4828	0.3028	39.9	145.0
Cod oil	0.923	1.4810	0.3083	39.6	154.0
Blown 24 hours	0.934	1.4828	0.3057	40.1	141.0
Coal-fish liver oil	0.921	1.4786	0.3077	39.7	153.0
Blown 24 hours	0.931	1.4794	0.3048	39.9	130.0
Herring refuse oil	0.923	1.4784	0.3069	40.0	146.0
Blown 18 hours	0.928	1.4795	0.3059	40.2	132.0
Fresh herring oil	0.923	1.4780	0.3067	40.0	145.0
Blown 18 hours	0.932	1.4805	0.3049	40.2	130.0
Pale seal oil	0.932	1.4795	0.3045	39.9	121.5
Blown 24 hours	0.968	1.4820	0.2945	40.7	91.5
Whale oil	0.933	1.4762	0.3024	44.5	121.0
[1]Blown 24 hours	0.950	1.4773	0.2976	47.5	86.0
Shark liver oil	0.910	1.4750	0.3094	40.0	120.0
Blown 24 hours	0.916	1.4762	0.3080	40.1	103.0
Arctic sperm oil	0.885	1.4670	0.3135	40.5	80.0
Blown 24 hours	0.892	1.4677	0.3115	40.6	71.0
Linseed oil	0.932	1.4825	0.3062	39.5	174.0
Blown 24 hours	0.944	1.4843	0.3032	39.6	151.0
Linseed oil	0.930	1.4817	0.3064	39.6	164.5
Blown 24 hours	0.943	1.4840	0.3034	39.8	139.5
Refined rape oil	0.911	1.4748	0.3090	40.0	102.0
Blown 24 hours	0.922	1.4758	0.3058	40.0	86.0
Cottonseed oil	0.920	1.4745	0.3058	40.0	106.0
Blown 24 hours	0.936	1.4759	0.3013	40.0	94.0
Olive oil	0.912	1.4695	0.3056	40.1	86.0
Blown 24 hours	0.918	1.4701	0.3040	40.2	76.0
English press'd castor	0.958	1.4800	0.2965	40.3	83.0
Blown 24 hours	0.967	1.4807	0.2941	40.3	68.0
Australian oleine oil	0.892	1.4620	0.3082	40.1	88.0
Blown 24 hours	0.900	1.4628	0.3059	40.2	73.0
Lard oil	0.914	1.4697	0.3051	40.0	78.0
Blown 24 hours	0.925	1.4713	0.3023	40.4	66.0

Fahrion's Method for Oxidised Oils.—(*Zeits. angew. Chem.*, 1898, 781–785).—From 2 to 3 grm. of the sample are saponified with 10 c.c. of 8% alcoholic potassium hydroxide on a boiling water-bath. The alcohol is evaporated, the soap dissolved in hot water, and the solution decomposed with hydrochloric acid in a separating funnel, shaken with 25 c.c. of petroleum spirit, and allowed to stand overnight, when the liquid will separate into two clear layers, with a stratum of solid hydroxy-fatty acids at the line of junction. As the non-volatile acids are all contained in the petroleum layer, it is unnecessary to again shake out the aqueous layer with petroleum spirit. After running off the lower liquid the petroleum layer is withdrawn from above, leaving the hydroxy-fatty acids in the funnel. If the quantity is considerable, it may enclose unoxidised fatty acids; and it is therefore advisable to dissolve the mass in a dilute solution of soda or ammonia, and repeat the treatment with petroleum spirit after acidifying with hydrochloric acid.

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[1] In the dispersion, after oil has been blowing 16 to 24 hours, it is almost impossible to get a proper or definite dividing line.

The united petroleum spirit extracts are evaporated, and the residue, consisting of the unoxidised fatty acids and unsaponifiable matter, dried to constant weight (1). It is then dissolved in 25 c.c. of 90% alcohol and titrated with seminormal alkali, the mg. of KOH being calculated on the original oil. The number thus obtained, which the author terms the "inner saponification value," furnished a measure of the non-volatile and unoxidised fatty acids.

The neutral alcoholic solution is extracted with petroleum spirit, the extracts washed with alcohol, the petroleum spirit evaporated, and the residue of unsaponifiable matter dried and weighed (2).

The difference between (1) and (2) gives the quantity of non-volatile fatty acids, the molecular weight of which can be calculated from the inner saponification value.

The hydroxy-fatty acids left in the separating funnel are dissolved in hot alcohol, the solvent evaporated, the residue dried to constant weight, ignited, the ash deducted, and the difference taken as the hydroxy-fatty acids (3).

The sum of $1+3$ gives the Hehner value.

The following results were thus obtained with cottonseed oil and three oxidation products, which were prepared by exposing the oil on wash-leather for 8 and 12 days, respectively. The leather was cut into fragments and extracted with cold petroleum spirit, furnishing products A and B. The second leather still contained a considerable amount of product insoluble in petroleum spirit, which was subsequently extracted from it with cold ether (B_1). It was a thick yellow oil, soluble in alcohol.

	Cotton-seed	A	B	B_1
Iodine value	108.8	55.4	46.3	29.1
Acid value	2.2	13.3	13.8	33.4
Saponification value	190.4	223.1	227.5	271.3
Inner saponification value	186.9	128.8	128.9	74.4
Hehner value	94.22	85.34	83.62	74.20
Unsaponifiable matter, %	1.10	1.11	1.28	0.72
Oxy-fatty acids, %	0.27	20.70	19.43	37.72
Non-volatile fatty acids, %	92.85	62.53	62.91	35.76
Molecular weight of fatty acids	278.1	276.2	273.3	269.1
M. p. of fatty acids	35–36°	45–46°	46°	51°

That volatile acids are produced during the oxidation process is shown by the decrease in the Hehner and inner saponification values. The increase in the amount of unsaponifiable matter in B is only apparent, since B and B_1 are both fractions of the same oxidation products, and the greater proportion of unsaponifiable matter was removed by the preliminary treatment with petroleum spirit which gave B.

The general conclusion arrived at on this point is that during the oxidation of fats and oils the unsaponifiable matter remains intact, and new substances are not formed from it.

Unlike the oxy-fatty acids of liver oils (*Zeits. angew. Chem.*, 1891, 643), those of cottonseed oil are completely soluble in ether.

The foregoing method of analysis affords a means of examining the course of oxidation during the drying of linseed oil, and is also applicable to the examination of unoxidised fats and oils, as is seen in the following examples:

	Ox tallow	Olive oil	Butter fat
Saponification value	193.9	188.4	225.9
Inner saponification value	193.8	188.1	185.2
Hehner value	95.58	95.25	87.60
Unsaponifiable matter	0.11	0.98	0.24
Oxy-fatty acids	0.13	0.18	0.14
Non-volatile fatty acids	95.34	94.07	87.22
Molecular weight of fatty acids	275.0	280.1	263.7

From these results it is obvious that when, as in the case of tallow and olive oil, the total saponification and inner saponification values are nearly identical, the amount of volatile or of oxy-fatty acids must be insignificant. Butter fat, on the other hand, by reason of its volatile acids, shows a considerable difference (40.7) between the two values, and the Reichert-Meissl value (36.3 for 5 grm.) can be calculated from this difference. This calculated value is higher than the normal, owing to the fact that the Reichert value only represents a portion of the total volatile acids.

In addition to the usual methods for determining the presence of blown oils in lubricants, Marcusson[1] proposes to distinguish between rape or cottonseed oils, using a method based on the different behaviour of the lead salts of the fatty acids from the oxidised oils toward petroleum ether. Also by the behaviour toward petroleum ether of the fatty acids separated from the lead salts insoluble in ether. He gives the following table:

	Fatty acids obtained from lead salts in ether		
	Total amount	Amount soluble in petroleum ether	Amount insoluble in petroleum ether
Coml. blown rape oil............	1.2%	1.2%	0.0%
Coml. blown rape oil............	14.5%	5.7%	8.8%
Blown rape oil prepared by author	20.6%	8.7%	11.9%
Coml. blown cottonseed oil........	32.9%	23.3%	9.6%
Blown cottonseed oil prepared by author	45.8%	32.5%	13.3%

The percentages refer to the weight of oil used for the preparation of the lead salts of the fatty acids. The fatty acids from blown cottonseed oil melted at 54 to 56°, while those from blown rape oil were oily and semifluid.

Lewkowitsch (*lot. cit.*) is of the opinion that differentation by means of the m. p. of the fatty acids would yield more information than the comparison of the solubility of the lead salts in petroleum ether.

The writer wishes to thank Mr. J. Gould Bearn, M. Sc., of Hull, for kindly reading proofs and supplying certain figures which are included in this section.

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[1] *Chem. Rev. Fett-Harz-Ind.*, 1905, 12, 290.

HIGHER FATTY ACIDS.

BY W. ROBERTSON, A. R. C. S.

The term "fatty acids," used in its widest sense, includes the whole series of homologous acids of which formic acid is the lowest member, together with the unsaturated acids of the acrylic or oleic series, the peculiar acids obtained on hydrolysis of castor and drying oils and many others.

The lower members of the saturated series (formic, acetic, etc.) have been considered in Vol. 1.

The following tables give some particulars of fatty acids of interest or importance as constituents of fixed oils or fats. Information regarding the analytical characteristics of caprylic, pelargonic, and capric acids will be found in volume 1. Palmitic, stearic, and oleic acids are described at length in subsequent sections as they are of frequent occurrence. Further information regarding arachidic, erucic, linoleic, and ricinoleic acids will be found in the sections treating of the oils of which they are especially characteristic—namely, arachis oil, rape oil, linseed oil, and castor oil.

Methods for the detection and estimation of the lower members of the acetic series are described in Vol. 1.

The m. p. and b. p. of acids of the stearic series rise with increase in the number of carbon atoms. The higher members cannot be distilled under the ordinary atmospheric pressure without suffering more or less decomposition, but may be distilled unaltered under diminished pressure. The table shows the b. p. of some of the stearic series under diminished pressure.

Similarly, oleic acid may be distilled in a vacuum or in a current of superheated steam at 250°, without material alteration; but if distilled in contact with air it is partially decomposed, with formation of carbon dioxide, paraffinoid hydrocarbons, and acetic, caproic, caprylic, capric, sebacic, and other acids.

In the following tables the acids of the different series are arranged together. Their relationship is evident from the following list of the acids containing 18 carbon atoms in the molecule:

$C_{18}H_{36}O_2$, stearic acid.
$C_{18}H_{34}O_2$, oleic acid; elaïdic acid.
$C_{18}N_{32}O_2$, linoleic acid; stearoleic acid.
$C_{18}H_{30}O_2$, linolenic acid; isolinolenic acid.
$C_{18}H_{34}O_3$, ricinoleic acid; isoricinoleic acid.
Ricinelaidic acid; rapic acid.

A. HIGHER ACIDS OF THE ACETIC OR STEARIC SERIES, $C_nH_{2n+1}\ CO_2H$.

Name	Formula	Chief sources	M. p.	B. p.	Sp. gr.	Other characteristics
Caprylic (octoic) ..	$C_8H_{16}O_2$	Coconut oil and butter fat.	16.5°	236°/760 mm. 123.5–124.3°/10 mm.	0.910 20°/4°	Crystallises in needles or plates. Soluble in 400 parts of boiling water, mostly deposited on cooling, readily soluble in alcohol, ether, and benzene. Barium salt moderately soluble.
Pelargonic (nonoic).	$C_9H_{18}O_2$	....	12.5°	186°/100 mm.	0.911 12°/4°	
Capric	$C_{10}H_{20}O_2$	Butter fat, codliver and coconut oils.	31.3–31.4°	268–270°/760 mm. 199.5–200°/100 mm. 153–154°/13 mm.	0.930 (37°) 0.8858 40°/4°	Crystallises in plates, slightly soluble in water; easily in alcohol and ether. Barium salt dissolves in boiling water.
[1] Umbellulic	$C_{11}H_{22}O_2$	*Nut of Umbellularia californica.*	21–23°	275–280°/760 mm. 212°/100 mm.	....	
Lauric	$C_{12}H_{24}O_2$	Synthetic .... Coconut, palmnut croton, laurel oils.	28° 43.6°	225°/100 mm. 176°/15 mm.	0.883	Crystallises in scales from fused state. Lead salt insoluble in ether and sparingly soluble in alcohol.
Ficocerylic	$C_{13}H_{26}O_2$	Wax of wild fig tree......	57°	....	....	
Myristic	$C_{14}H_{28}O_2$	Coconut and dika oils, nutmeg butter and spermaceti.	53.8°	250 5/100 121° vacuo	0.8584 60°/4°	Insoluble in water, lead salt insoluble in ether, soluble in alcohol.
Isocetic	$C_{15}H_{30}O_2$	Curcas oil	55°	....	....	Doubtful.
Palmitic	$C_{16}H_{32}O_2$	Palm oil and most fats...	62.6°	339–356°/760 mm. (decomp.) 215°/15 mm. 138–139° vacuo	0.8527 62.6°	See "Palmitic Acid."
Stearic	$C_{18}H_{36}O_2$	Most fats	69.32°	359–380°/760 mm. 291°/100 mm. 232°/15 mm.	0.845° (m. p.)	See "Stearic Acid."
Arachidic	$C_{20}H_{40}O_2$	Arachis oil	77°	....	....	Sparingly soluble in cold, easily soluble in hot alcohol. Lead salt insoluble in ether.
Behenic	$C_{22}H_{44}O_2$	Oil of ben	83–84°	306°/60 mm.	....	
Lignoceric	$C_{24}H_{48}O_2$	Arachis oil, beech-wood tar.	80.5°			
Pisangcerylic.....	$C_{24}H_{48}O_2$	Pisang wax	71°			
Hyenic	$C_{25}H_{50}O_2$	Secretion of anal glands of striped hyena.	77–78°			
Cerotic	$C_{26}H_{52}O_2$	Beeswax and carnaüba wax.	78.5°			
Melissic	$C_{30}H_{60}O_2$	Beeswax	90°			

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[1] There is some doubt as to this acid and other acids containing an odd number of carbon atoms occurring in nature.

B. HIGHER ACIDS OF THE ACRYLIC OR OLEIC SERIES, $C_nH_{2n-2}O_2$ *or* $C_nH_{2n-1}CO_2H$

Name	Formula	Chief sources	M. p.	Other characters	Insomeric (or polymeric) acids produced by the action of nitrous acids on natural acids
Hypogeic	$C_{16}H_{30}O_2$	Arachis oil	33°	Forms colourless crystals, readily soluble in alcohol and ether. Combines with Br_2. Yields gaïdic acid with nitrous acid and sebacic acid on distillation. Lead salt soluble in ether.	*Gaïdic acid* forms a crystalline mass m. p., 39°. Volatilises almost unchanged. Readily soluble in alcohol. Combines with Br_2.
Physetoleic		Said to exist in sperm oil.	30°	Differs from hypogeic acid in not yielding sebacic acid on distillation.	
Asellic	$C_{17}H_{32}O_2$	Said to exist in sardine oil.			
Oleic	$C_{18}H_{34}O_2$	The majority of fatty oils form the olein of commerce.	14°	See "Oleic Acid."	*Elaïdic acid*, produced by action of nitrous acid on oleic acid. Pearly plates m. p., 51–52°, and distilling almost unchanged.
Isoöleic		By distillation of hydroxystearic acid.	45°	Soluble in alcohol and ether. Unites with Br_2. Behaves like oleic acid, when fused with alkali. Lead salts less soluble in ether than lead oleate.	
Rapic		Rape oil (Zellner, *J. Soc. Chem. Ind.*, 1896, 15, 661).	Liquid		
Dœglic	$C_{19}H_{36}O_2$	Said to exist in bottle-nose oil.	16°	Resembles oleic acid	*Dœglaïdic acid*, produced by action of nitrous acid on oleic acid.
Jecoleic		Said to exist in cod-liver oil.			
Erucic or Brassic	$C_{22}H_{42}O_2$	Rape oil, black and white mustard oils.	33–34°	Crystallises from alcohol in long laminæ or needles. Combines with Br_2. Lead salt less soluble in ether than is lead oleate. Yields acetate and arachidate when fused with potassium hydroxide.	*Erucaïdic* or *Brassaïdic acid*, produced by action of nitrous acid on erucic acid; m. p., 65°. Lead salt nearly insoluble in warm ether.

C. HIGHER ACIDS OF THE PROPIOLIC OR LINOLEIC SERIES, $C_nH_{2n-4}O_2$.

Name	Formula	Chief sources	M. p.	Other characters	Isomeric acids
Eleomargaric ...	$C_{17}H_{30}O_2$	Japanese wood oil...	48	On exposure to light the solution in alcohol or ether deposits isomeric eleostearic acid.	*Eleostearic acid;* m. p. 71°.
Linoleic.........	$C_{18}H_{32}O_2$	Linseed and other drying oils.	below −18°	Liquid at low temperature. Not solidified by nitrous acid. Yields stearic acid by hydrogenation and *sativic acid* when oxidised in alkaline solution. Combines with Br_4. Lead salt soluble in ether. Absorbs oxygen rapidly from air. Sp. gr. 0.9206 (14°).	*Tariric acid* found in fat of seeds of Guatemalan *Picraminia.* M. p., 50.5°. Combines with Br_4.

D. HIGHER ACIDS OF THE LINOLENIC SERIES, $C_nH_{2n-6}O_2$.

Name	Formula	Chief sources	Other characters
Linolenic	$C_{18}H_{30}O_2$	Linseed and other drying oils.	Liquid; very oxidisable. Combines with Br_6. Forms linusic acid, m. p., 203° when oxidised in alkaline solution. Lead salt soluble in ether.
Isolinolenic		Said to exist in linseed oil, but has not been isolated from it.	Resembles linolenic acid, but forms isolinusic acid, m. p., 173°–175° when oxidised in alkaline solution.

E. HIGHER ACIDS OF THE HYDROXYOLEIC OR RICINOLEIC SERIES, $C_nH_{2n-2}O_3$.

Name	Formula	Chief sources	Other characters	Isomeric acid
Ricinoleic........	$C_{18}H_{34}O_3$	Castor and curcas oils..	Thick oily liquid, sp. gr. 0.940 (15°). M. p. 4–5°, optically active.	*Ricinelaïdic acid*, produced by action of nitrous acid on ricinoleic acid. M. p., 50°. Crystallises from alcohol in silky needles. Combines with Br_2. Lead salt, m. p. 100°, is soluble in ether.
Isoricinoleic......		Castor oil	Resembles ricinoleic acid	

General Properties of the Fatty Acids.—The lower members of the fatty acid series are soluble in water, capric and lauric acids are slightly soluble in boiling water, the higher acids are insoluble. They are all, however, soluble in hot alcohol, ether, and petroleum spirit. The alcoholic solutions all give more or less marked acid indications, and both in solution and in the molten state decompose the carbonates of the alkali metals. The interaction between an alkaline hydroxide and a fatty acid in water is not a complete one, free acid and free alkali existing as well as the resultant "soap." The fatty acids of the different series formulated in the foregoing tables present certain marked points of difference and general characters of interest of which the following are the chief:

A. The higher acids of the *stearic series* are solid at the ordinary temperature. They do not give additive compounds with bromine, nor do they react with Hübl's reagent; in other words, they are saturated compounds. They do not undergo change when heated with potassium hydroxide at 300° or with phosphorus and hydriodic acid. The lead salts are insoluble in ether.

B. The higher members of the *oleic* or *acrylic* (from acrylic acid, the lowest member) series have lower m. p. than the corresponding acids of the stearic series, and are unsaturated compounds absorbing two atoms of the halogens or hydrogen. They interact with Hübl's reagent to give analogous compounds. The higher acids when in contact with sodium amalgam do not take up hydrogen to form saturated acids (Lewkowitsch, *J. Soc. Chem. Ind.*, 1897, **16**, 390), but colloidal palladium or platinum-black reduces oleic acid or unsaturated glycerides at the ordinary temperature (Fokin, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 607–609; Paal and Roth, *Ber.*, 1908, **41**, 2282–2291). The reduction may also be carried out with phosphorus and fuming hydriodic acid at 200 to 220°.

When heated carefully with potassium hydroxide at 300°, potassium acetate and the potassium salt of an acid of the stearic series containing 2 carbon atoms less than the original unsaturated acid employed are obtained; when heated rapidly with this alkali, sebacic acid, $C_{10}H_{18}O_4$, is also obtained from certain of these acids. Oleic acid and some of its homologues, when treated with nitrous acid at ordinary temperatures, are transformed into isomerides of higher m. p. Oxidation with potassium permanganate in alkaline solution leads to the formation of acids of the dihydroxystearic series. The lead salts are soluble in ether; lead elaidate is, however, only very slightly soluble, like lead stearate, and this property, when utilised in separating lead salts of the unsaturated from those of the saturated series, requires to be used with caution.

C. The acids of the *linoleic series* form additive compounds with 4 atoms of bromine and interact with a larger proportion of Hübl's reagent than do acids of the oleic series. They absorb oxygen from the air, and oxidation of linoleic acid in the cold with dilute potassium permanganate leads to the formation of sativic or tetrahydroxystearic acid. They are not affected by nitrous acid. The lead salts are soluble in ether.

D. *Linolenic acid* combines with 6 atoms of bromine or iodine and readily absorbs oxygen. Nitrous acid does not produce solid isomerides. Lead linolenate is easily soluble in ether.

E. *Ricinoleic acid* combines with 2 atoms of bromine, does not absorb oxygen on exposure to the air, is gradually converted by nitrous acid into a solid stereoisomeride. Its lead salt is soluble in ether. Oxidation with potassium permanganate gives two trihydroxystearic acids.

Recognition and Estimation of Fatty Acids.—The methods available for the detection and to some extent for the estimation of the higher fatty acids are based on the characters just described. In many cases it is unnecessary to effect actual separation of the fatty acids in a mixture, it being sufficient to ascertain the joint amount, or to ascertain indirectly and approximately the proportion of the acids of different origin known to be present.

Methods not Involving Separation.—*a.* Free fatty acids can be accurately estimated by titration in alcoholic solution with standard alkali, using phenolphthaleïn to indicate the point of neutrality. The mode of operating is fully described on page 9. A mixture of 1 part of alcohol to 2 of amyl alcohol as solvent is recommended by Swoboda (*Chem. Zeit.*, 1900, **24,** 285) as it avoids the formation of two layers. Neutral substances—*e. g.*, fats and hydrocarbons—do not interfere. Mineral acids and acid salts must first be removed by agitation with water, or estimated by titration in alcoholic solution with methyl-orange as indicator, and resin acids must be separated or duly allowed for. In the case of a mixture of several fatty acids the result is best expressed in terms of the principal or most characteristic acid present, and in most cases such a mode of statement gives a close approximation to the total of the free fatty acids present.

Conversely, when the substance under examination consists wholly of a mixture of fatty acids, titration with standard alkali suffices to ascertain the mean combining weight of the mixed acids. This is found by dividing the number of mg. of fatty acids employed for the titration by the number of c.c. of normal alkali required for neutralisation.

In cases of a mixture of two homologous acids, the nature of which is known or can be ascertained by other means, the result of the titration gives the means of ascertaining the proportions in which the two constituent acids exist in the mixture. An example of the application of the method to this purpose is given on page 383.

b. Köttstorfer's method (page 15) may be regarded as a process of approximately ascertaining the mean combining weight of the fatty acids of an oil, fat or wax without actually isolating them. 3 c.c. of a 2% alcoholic solution of alkali blue 6B Meister, Lucius and Brüning) can be substituted with advantage for phenolphthaleïn, when the oils give dark coloured solutions. This solution is red with alkali, blue with acid. The saponification values obtained are fairly constant, and are important in determining the nature of an oil or fat; but, as a means of ascertaining the mean combining weight of the acids, the method is only applicable to oils which yield 95% of fatty acids on hydrolysis.

Tortelli and Pergami (*Chem. Rev., Fett. Harzind.*, 1902, 182) have stated that the acids from oils and fats contain quantities of anhydrides or lactones which are not attacked by dilute alkali in the cold, and therefore too high a molecular weight is found. The true molecular weight is found by heating with excess of N/2 alkali, and titrating back with hydrochloric acid. The further statement is made that in the case of fresh samples the number obtained is only a few units greater than the neutralisation value, but that in old samples the anhydride is quite important. A few of their results are tabulated.

MEAN MOLECULAR WEIGHT OF FATTY ACIDS.

	Insoluble fatty acid		Difference	Mean molecular weight calculated from		Difference
	Neutralisation value	Saponification value		Neutralisation value	Saponification value	
Oleic acid fresh from olive oil	199.5	201.4	1.9	281.2	278.5	2.7
Oleic acid, 2 years old, from beef fat	191.0	202.8	11.8	293.8	276.6	17.2
Oleic acid, 5 years old, commercial	181.6	189.3	7.7	308.2	296.5	11.7
Almond oil, fresh	195.8	203.0	7.2	286.5	278.5	8.2
Almond oil, 2½ years old	196.0	202.2	6.2	286.2	277.5	8.7
Linseed oil, fresh	194.6	201.8	7.2	288.2	277.9	10.3
Linseed oil, 3 years old	191.5	205.4	13.9	292.8	273.2	19.6
Cottonseed oil, fresh	200.9	203.1	2.2	279.2	276.2	3.0
Cottonseed oil, 2½ years old	194.3	204.5	10.2	288.7	274.3	14.4
Rape oil, fresh	176.6	181.2	4.6	317.7	309.6	8.1
Rape oil, 2 years old	178.3	182.5	4.2	314.6	307.4	7.2
Rape oil, 5 years old	176.1	181.4	5.3	318.8	309.1	9.1
Arachis oil, fresh	195.8	203.0	7.2	286.5	278.3	8.2

Lewkowitsch (*Jahrb. Chem.*, 1901, **11**, 359) carefully repeated this work and the results obtained were sometimes in agreement with those of Tortelli and Pergami; in other cases, however, the differences were within the limits of experimental error and even negative differences were found. The differences are probably due to the formation of lactones from hydroxy-fatty acids, but may also result from the formation of anhydrides from the acids by the action of heat.

c. The titration of a mixture of oleic acid with acids of the stearic series by means of Hübl's solution (page 30) allows the former constituent to be determined with considerable accuracy. As 282 parts of oleic acid, $C_{18}H_{34}O_2$, absorb 254 parts of iodine, the iodine value divided by 0.9 gives the percentage of *oleic acid* present. It is even possible to ascertain the percentage of oleic acid when another unsaturated acid like linoleic acid is present. The latter acid absorbs four atoms of iodine and as the molecular weights of the two unsaturated acids are very nearly the same (282 : 280), linoleic acid may be regarded as absorbing twice as much iodine as oleic acid. Hence, if 90 be subtracted from the observed iodine value of the mixed acids, and the difference divided by 0.9, the dividend will be the percentage of linoleic acid in the mixture. If acids of the stearic series are also present, they must be separated or duly allowed for in making the calculation. If the percentages of stearic, oleic and linoleic acids are represented, respectively, by s, o, and l and the iodine value by A, then, the value of s being known, the liquid acid percentages are:

$$o = 200 - 1.11A - 2s; \text{ and } l = 100 - s - o.$$

d. Useful information respecting the fatty acids present can be obtained from the m. p. or solidifying-point of the substance. When the mixture consists merely of two acids of the stearic series, the result affords a means of approximately ascertaining their relative proportions. The m. p. of some mixtures of the acids of the stearic series, as found by Heintz, are given in a tabular form on page 385 *et seq*. The m. p. and solidifying-points of the fatty acids from different fixed oils are more or less characteristic of their origin, as also are the sp. gr. and mean combining weights.

The following table gives data obtained in Allen's laboratory. The fatty acids were prepared as follows: The oil was saponified with alcoholic potassium hydroxide, the alcohol evaporated, the residual soap dissolved in hot water and decomposed by dilute sulphuric acid. The liquid having been well boiled, the separated fatty acids were filtered through paper. With sperm and bottlenose oils the higher alcohols were removed by agitating the solution of the soap with ether, the ethereal layer separated, and the ether that remained in the soap solution removed by warming before liberating the fatty acids. In the case of the other oils the trifling proportion of unsaponifiable matter was ignored.

Kind of oil	Characters of separated insoluble fatty acids				
	Sp. gr.		M. p.	Solidifying point	Combining weight
	At 15.5°	At 98–99°			
Olive oil	solid	0.8430	26.6°	21.0°	279.4
Arachis oil	solid	0.8460	29.5°	28.0°	281.8
Rape oil	solid	0.8438	19.5°	18.5°	321.2
Cottonseed oil (pressed)	solid	0.8467	35.0°	32.0°	287.2
Sesame oil	solid	......	23.0°	18.5°	286.5
Linseed oil	0.9233	0.8612	24.0°	17.5°	307.2
Castor oil	0.9509	0.8960	....	....	306.6
Palm oil	solid	0.8369	50.0°	45.5°	269.6
Coconut oil	solid	......	24.0°	20.5°	.....
Japan wax	solid	0.8482	56.0°	53.0°	265.3
Myrtle wax	solid	0.8370	47.5°	46.0°	243.0
Lard	solid	......	44.0°	39.0°	278.0
Northern whale oil	0.9076	0.8595	....	....	298.7
Sperm oil	0.8990	......	....	....	289.4
Bottlenose oil	0.8965	......	....	....	294.6

The following results have been communicated by other observers:

Source of fatty acids	Combining weight	Observer
Tallow, lard, or olive oil	270–285	C. R. Alder Wright.
Castor oil	290–295	C. R. Alder Wright.
Coconut oil	196–204	C. R. Alder Wright.
Palm oil	273	A. Norman Tate.
Palmnut oil	211	E. Valenta.
Cottonseed oil	275	E. Valenta.
Sesame oil	286	E. Valenta.

The following table gives the m. p. and solidifying-points of the fatty acids ascertained by several observers:

Source of fatty acids	M. p.	Solidifying-point.	
		Various methods	Titer test (Lewkowitsch)
Olive oil	21–30°	17–26.4°	16.9–26.4°
Almond oil	13–14°	5–12° (t)	9.5–11.8°
Arachis oil	27–30°	24–31°	28.1–29.2°
Rape oil	16–21°	12–18°	11.7–13.6°
Cottonseed oil	34–40°	32–40°	32.2–37.6°
Sesame oil	24–32°	18–28°	21.2–23.8°
Nigerseed oil	25–27°	....	....
Poppyseed oil	20–21°	15.5–17°	....
Linseed oil	17–24°	13–20°	19.0–20.6°
Hempseed oil	17–28°	14–16°	15.6–16.6°
Walnut oil	15–20°	16–17°	....
Castor oil	13°	2–3°	....
Palm oil	48–50°	36–45.5°	35.8–45.4°
Palmnut oil	21–28°	....	20 –25.5°
Cacao butter	48–53°	46–51°	48 –48.27°
Nutmeg butter	42.5°	36–40°	35.5–35.95°
Shea butter	40–56°	38–54°	53.75–53.8°
Coconut oil	24–25°	16–25°	21.2–25.2°
Japan wax	56–62°	53–59°	58.8–59.4°
Myrtle wax	47.5°	46°	....
Lard oil	33–38.5°	....	....
Lard	37–47°	32–43°	41.45–42°
Compounded lard	39–43°	....	....
Tallow, mutton	41–49°	....	40.15–48.3°
Tallow, beef	41–47.5°	....	37.9–46.25°
Margarine	42°	40°	....
Butter fat (insoluble acids)	38–42°	37–38°	....
Sperm oil	13°	11–12°	11.1–11.9°
Whale oil	14–18°	23–24°	22.9–23.9°

The differences in the m. p. and solidifying-points are in great measure due to different methods of observation.

The figures have, in some instances, considerable practical value. Thus, the high m. p. of the fatty acids obtained on saponification distinguishes cottonseed oil from nearly all other liquid fixed oils of vegetable origin, and enables its presence to be inferred in admixture with other oils; the m. p. of the acids from cacao butter is remarkably constant, and is sometimes useful as a test of the purity of the fat; while the solidifying-point of the acids from palm oil affords a practical indication of the value of the sample to the candle manufacturer. The same remark applies to the fatty acids of tallow, and a table has been constructed by Dalican (page 212) by which the proportion of oleic and solid fatty acids which a sample of tallow will yield can be deducted from the solidifying-point of the mixed acids.

Separation of Mixed Fatty Acids.—The actual *separation* of mixed fatty acids is often a problem of extreme difficulty, and indeed cannot in all cases be satisfactorily solved in the present condition of chemistry. Methods for effecting the recognition and separation of the lower members of the stearic series will be found in Volume 1. The principles which have been applied to the fatty acids enumerated in the tables on page 372 *et seq.* include the following:

1. The mixed fatty acids are well washed by agitation with hot water, when those containing 10 atoms or fewer of carbon are dissolved. This process is applied to the analysis of the fatty acids from butter-fat.

2. The mixed fatty acids obtained by treating the soaps with a moderate excess of dilute sulphuric acid are distilled with water, either with or without the aid of a current of steam (page 19). This method allows a more or less complete separation of the homologues up to lauric acid from the higher members of the stearic series. The soluble acids obtained in 1 are not necessarily the same as in 2.

3. The acids are converted into barium salts, and the precipitate treated with water or alcohol. The barium salts of lower members up to capric acid can be dissolved out by boiling water (page 297).

4. The alcoholic solution of the acids is precipitated by magnesium acetate. By operating fractionally some useful separations may be effected (see below).

5. The acids are converted into lead salts, which are then treated with ether or alcohol. An application of this principle enables oleic

acid and its homologues to be separated from the higher acids of the stearic series.

6. Fractional distillation, fractional fusion and pressure, and fractional solution in or crystallisation from alcohol or other solvents are other processes employed for the separation of the fatty acids.

No precise method of *separating* oleic acid and its homologues from linoleic acid has hitherto been devised. Possibly one might be based on the conversion of the acids of the oleic series into isomers of higher m. p. and modified properties by means of nitrous acid. Methods 1, 2, and 3 have already been sufficiently described, and those under 6 do not require further notice. Methods 4 and 5, however, are described in detail below.

Separation of the Higher Fatty Acids of the Stearic Series.—The higher homologues of the stearic series can be separated from the lower members by treatment with hot water or distillation in a current of steam, and from the insoluble and non-volatile acids of other series by treatment of the lead soaps with ether. By proper application of these methods there may be obtained a mixture of solid, non-volatile homologues of stearic acid, which, according to its origin, may contain more or less lauric, myristic, palmitic, stearic, arachidic, and other less frequently occurring acids of the series. The separation of these homologues is extremely difficult, and a quantitative estimation of several immediate homologues occurring in a mixture is especially so. Advantage may be taken of the limited solubility of *arachidic acid* in alcohol to effect its separation, as is done in Renard's process for the detection of earthnut oil (page 93); and indeed the solubility of the homologues in alcohol rapidly increases with a diminution of the number of carbon atoms in the acid. For the actual *separation* of the higher homologues of the stearic series from each other, however, the most satisfactory method is that of Heintz (*J. pr. Chem.*, 1855, **66**, 1), based on fractional precipitation of the alcoholic solution of the acids with magnesium acetate. This salt precipitates acids of the stearic series more easily than it does oleic acid and its homologues, and, of the different homologues of the stearic series, those of the highest molecular weights are thrown down first. In practice, 40 grm. of the mixed fatty acids should be dissolved in such a proportion of hot alcohol that nothing will separate on cooling, even at 0°, and the hot liquid treated with a boiling alcoholic solution of 1.5 grm. of magnesium acetate. The liquid is well agitated and allowed to become cold, when the precipitate is filtered off and the filtrate treated with a fresh quantity of alcoholic magnesium acetate. This second precipitate is similarly separated, and the treatment repeated as long as anything is thrown down. To induce precipitation of the lower homologues, it becomes necessary to render the liquid alkaline with strong ammonia before adding magnesium acetate, and to allow the solution to stand in the cold for 24 hours before filtering. The first fractions of the precipitate contain magnesium stearate and any higher homologues, the succeeding portions will consist chiefly of magnesium palmitate, and the last will probably contain myristate; but a portion of the myristic acid, the whole or nearly the whole of the lauric acid, and any oleic acid which may be present will remain in solution, and may be precipitated by addition of lead acetate after neutralising the excess of ammonia with acetic acid. The precipitate should be filtered off, washed with cold dilute alcohol, and, if oleate be present, treated with ether. The purified lead precipitate and the several magnesian precipitates should be washed with cold alcohol, pressed, and decomposed by hot dilute hydrochloric acid, the liberated fatty acids being washed free from mineral acid by repeated agitation with hot water, and further treated as described on page 19. The details of the fractional precipitation should be modified to suit particular cases, and in some instances separation into a smaller number of fractions will suffice.

The several fractions of fatty acids thus obtained, after being weighed, if desired, should then be titrated with standard alkali in the manner described on page 9. 5 grm. of each fraction will be a suitable quantity, and this should be treated with about 30 c.c. of warm spirit (neutral) and titrated with N/2 sodium hydroxide, a few drops of a solution of phenolphthaleïn being employed as indicator, and an accurately divided burette being used. The mean combining weight of the acids constituting a fraction is found by dividing the number of mgs. of fatty acids employed by the number of c.c. of N/1 alkali required for their neutralisation. Thus, if 5 grm. of a fraction has been found to require 37.80 c.c. of N/2 for its neutralisation, the mean combining weight of the acids will be 264.5, for:

$$\frac{5000 \times 2}{37.8} = 264.5$$

As a rule, if the mixed fatty acids are divided into a sufficient number of fractions by precipitation with magnesium acetate, each fraction will contain only two homologues, in which case the result of the titration not only indicates the nature of the homologues present, but in many cases allows of their relative proportion being calculated. Thus, if, in the course of a systematic fractional precipitation as magnesium salts, a fraction of fatty acids is obtained having a mean combining weight of 264.5, it will almost certainly consist essentially of a mixture of stearic and palmitic acids, the former of which has the molecular weight 284 and the latter 256, the difference being 28. Hence every 1% of stearic acid in the mixture will raise the combining weight 0.28, or for every unit above 256 found for the combining weight of the fraction 3.57 of stearic acid should be calculated. As with all indirect methods of the kind, the results obtained are fairly satisfactory when both constituents are present in considerable proportions, but are of little value for mixtures in which one constituent very largely predominates.

The titration having been completed, the alcohol may be boiled off and the fatty acids again liberated and subjected to renewed fractional precipitation or crystallisation from alcohol. The products so obtained can be again titrated, and thus the progress of the isolation and purification of the fatty acids checked in a simple and satisfactory manner.

Valuable information respecting the composition of the various fractions obtained by the precipitation as magnesium salts is obtainable by determining the m. ps. of the fatty acids. For this purpose they should be purified by a single crystallisation from hot alcohol and dried by pressure between blotting-paper. Unfortunately, the m. p. of a mixture of two or more homologous fatty acids is not the mean of the m. ps. of the constituent acids. The m. ps. of various mixtures of solid fatty acids have been very carefully determined by Heintz, who has also noticed that the mixtures, on solidifying, crystallise in more or less characteristic forms or remain amorphous, according to the proportions in which the constituents are present. The following are some of the more important of the results of Heintz:

MIXTURES OF LAURIC ACID WITH ITS HIGHER HOMOLOGUES.

Lauric acid, %	With myristic acid		With palmitic acid	With stearic acid
	M. p.	Solidifying-point	M. p.	M. p.
100	43.6°	....	43.6°	43.6°
90	41.3°	36.0°	41.5°	41.5°
80	38.5°	33.0°	37.1°	38.5°
70	35.1°	32.3°	38.3°	43.4°
60	36.7°	33.5°	40.1°	50.8°
50	37.4°	35.7°	47.0°	55.8°
40	43.0°	39.0°	51.2°	59.0°
30	46.7°	39.0°	54.5°	62.0°
20	49.6°	44.5°	57.4°	64.7°
10	51.8°	47.3°	49.8°	67.0°
0	53.8°	....	62.0°	69.2°

MIXTURES OF MYRISTIC ACID WITH ITS HIGHER HOMOLOGUES.

Myristic acid, %	With palmitic acid		With stearic acid
	M. p.	Solidifying-point	M. p.
100	53.8°	....	53.8°
90	51.8°	45.3°	51.7°
80	49.5°	41.3°	47.8°
70	46.2°	43.7°	48.2°
60	47.0°	43.7°	50.4°
50	47.8°	45.3°	54.5°
40	51.5°	49.5°	59.8°
30	54.9°	51.3°	62.8°
20	58.0°	53.5°	65.0°
10	60.1°	53.7°	67.1°
0	62.0°	....	69.2°

MIXTURES OF PALMITIC ACID WITH STEARIC ACID.

Palmitic acid, %	Stearic acid, %	M. p.	Solidifying-point	Manner of solidification
100	0	62.0°	....	Crystalline scales.
90	10	60.1°	54.5°	Slender needles.
80	20	57.5°	53.8°	Very indistinct needles.
70	30	55.1°	54.0°	Amorphous, wavy, dull.
60	40	56.3°	54.5°	Large crystalline laminæ.
50	50	56.6°	55.0°	Large crystalline laminæ.
40	60	60.3°	56.5°	Amorphous, lumpy.
30	70	62.9°	59.3°	Slender needles.
20	80	65.3°	60.3°	Slender needles.
10	90	67.2°	62.5°	Crystalline scales.
0	100	69.2°	....	Crystalline scales.

Heintz also noticed that the addition of a third acid, even of higher m. p., to a mixture of two homologous acids causes a lowering of the m. p. This is shown in the following table:

Parts of palmitic acid added to lauric acid, 14; myristic acid, 6 parts	M. p.	Manner of solidification	Parts of stearic acid added to myristic acid, 14; palmitic acid, 6 parts	M. p.	Manner of solidification
0	35.1°	Amorphous, frond-like.	0	46.2°	Indistinct lamellæ.
1	33.9°	Amorphous.	1	45.2°	Amorphous.
2	33.1°	Amorphous.	2	44.5°	Amorphous.
3	32.2°	Amorphous.	3	44.0°	Amorphous.
4	32.7°	Amorphous.	4	43.8°	Amorphous.
5	33.7°	Amorphous.	5	44.6°	Amorphous.
6	34.6°	Amorphous.	6	45.6°	Amorphous.
7	35.3°	Amorphous.	7	46.0°	Amorphous.
8	36.0°	Amorphous.	8	46.5°	Amorphous.
9	37.3°	Indistinct minute needles.			
10	38.8°	Minute needles.			

The importance of ascertaining the solidifying points of mixtures of fatty acids has been latterly emphasised as the data obtained are more reliable than those derived from m. p. observations. Heintz obtained his values by the capillary method, but L. E. O. de Visser (*Rec. Trav. Chim.*, 1898, **17**, 182, 346), by using larger quantities and only allowing the temperature to fall slowly, obtained the following values for the solidifying points of mixtures of stearic and palmitic acids:

MIXTURE OF STEARIC AND PALMITIC ACIDS.

Stearic acid, %	Solidifying point	Stearic acid, %	Solidifying point	Stearic acid, %	Solidifying point
100	69.32°	48	56.40°	36	55.62°
90	67.02°	47	56.40°	34	55.38°
80	64.51°	46	56.39°	32	55.12°
70	61.73°	45	56.38°	30	54.85°
60	58.76°	44	56.36°	29	54.92°
55	57.20°	43	56.31°	25	55.46°
54	56.85°	42	56.25°	20	56.53°
53	56.63°	41	56.19°	15	57.80°
52	56.50°	40	56.11°	10	59.31°
51	56.44°	39	56.00°	0	62.62°
50	56.42°	38	55.88°		
49	56.41°	37	55.75°		

If these values are plotted on squared paper the curve so obtained has two points of inflection, one at 54%, the other at 47.5%, and the tangent at 47.5 is parallel to the axis of composition, thus the acids exist in "solid solution" here with only one form of crystalline aggregate. The lowest solidifying point is 54.817° at 29.76% stearic acid, but this is a mixture of two solid modifications.

The formation of "eutectic" mixtures in fatty acids has recently been examined by Carlinfanti and Levi-Malvano (*Gazzetta*, 1909, **39**, 353). In ascertaining the solidifying point, they take the beginning of crystallisation as the point of most value; in some instances, they also give the temperature when crystallisation is complete. When these two values are identical, the "solid solution" is identical with the liquid phase. Their values for stearic and palmitic acid mixtures are somewhat different from those of de Visser.

Stearic acid, %	Beginning of crystallisation	End	Stearic acid, %	Beginning of crystallisation	End	Stearic acid, %	Beginning of crystallisation	End
100	68.2°	....	60	57.65°	....	25	54.95°	....
95	67.10°	....	55	56.60°	....	20	55.75°	....
90	65.90°	61.50	52.5	56.00°	56.00	15	57.00°	....
85	64.75°	....	50	56.25°	56.25	10	58.40°	....
80	63.50°	....	45	56.10°	....	5	59.60°	....
75	62.15°	....	40	55.90°	....	0	61.00°	....
70	60.80°	57.00	35	55.15°	....			
65	59.30°	....	30	54.75°	54.75			

It will be noted that the solidifying points for the two pure acids are different from those of de Visser.

These authors have also examined stearic-oleic and palmitic-oleic mixtures, as well as mixtures of the three acids. With regard to the last the original should be consulted, as this is a very intricate case; information as to the composition of such mixtures may be derived, however, from the beginning of the solidification when taken in conjunction with the iodine value.

MIXTURES OF STEARIC AND OLEIC ACIDS.

Stearic acid, %	Beginning of crystallisation	End of crystallisation
100	68.2°	....
95	67.15°	....
85	65.40°	....
75	63.40°	57°
65	61.25°	....
55	58.65°	45°
46	55.95°	....
35	51.90°	34°
25	46.60°	....
15	34.25°	....
5	23.45°	....
0	9.00°	....

MIXTURES OF PALMITIC AND OLEIC ACIDS.

Palmitic acid, %	Beginning of crystallisation	Palmitic acid, %	Beginning of crystallisation
100	61.00°	40	46.25°
90	59.20°	30	41.60°
80	57.30°	20	35.00°
70	55.10°	10	24.80°
60	52.60°	0	9.0°
50	49.75°		

The m. p. of a mixture of two or more fatty acids taken alone is incapable of giving definite information; but if the observation is associated with other data useful inferences can be drawn. Thus the following mixtures of homologous fatty acids melt at nearly the same temperature, but may be distinguished by their combining weights, by titrating them in alcoholic solution with standard alkali and phenolphthaleïn (page 383).

Nature of mixed fatty acids				M. p.	Combining weight
Lauric	Myristic	Palmitic	Stearic		
30	70	..	..	46.7°	219.6
50	..	50	..	47.0°	228.0
..	70	30	..	46.2°	239.4
..	50	21	29	46.5°	250.0

This method of separation must, however, be used with care, especially if more than 2 acids are present in the mixture. Kreis and Hafner (*Ber.*, 1903, **36**, 2770) isolated in this way from lard an acid, $C_{17}H_{34}O_2$, m. p. 55–56°, but Holde, Ubbelohde and Marcusson (*Ber.*, 1905, **38**, 1250) have shown that not only this, but all the so-called daturic acids are mixtures of acids containing an even number of carbon atoms. Erroneous conclusions from the mixed m. p. determination may arise from the presence of an acid, *a*, of a higher m. p. than acids *b* and *c*, and fractional precipitation of such a mixture may give rise to several fractions of approximately the same m. p. and combining weight. These, however, may be resolved by repeated fractionation by means of magnesium acetate or distillation *in vacuo*.

The method of examining fatty acids, proposed by Benedikt and Ulzer, consisted in preparing the acetyl derivatives and then ascertaining the amount of alkali required for saponification.

It was at first assumed that only hydroxylated acids (*e. g.*, ricinoleic acid) form acetyl derivatives when treated in this way, but Lewkowitsch (*J. Soc. Chem. Ind.*, 1890, **9**, 660) showed that saturated acids, like capric, palmitic, stearic, and oleic acids, give considerable acetyl values. This is due to the formation of anhydrides of these acids, thus, $2C_{15}H_{21}CO_2H+(CH_3CO)_2O=(C_{15}H_{21}CO)_2O+2CH_3CO_2H$, the anhydride so formed, not being hydrolysed, by hot water, and even only partially hydrolysed when titrated in *cold* alcohol with alkali. Lewkowitsch recommended (*J. Soc. Chem. Ind.*, 1890, **9**, 846) that the acetyl actually combined with the hydroxylated fatty acid be estimated by hydrolysing with alcoholic potassium hydroxide, boiling off the alcohol and after liberation of the acid with sulphuric acid, distilling off the acetic acid and estimating its amount in the distillate. The value so obtained he called the "true acetyl value." The method devised by Lewkowitsch in 1897 (*J. Soc. Chem. Ind.*, 1897, **16**, 503), is now in general use; it is described on p. 33.

Separation of Acids of the Stearic Series from Fatty Acids of Other Series.—The higher homologues of the stearic series of fatty acids being solid at ordinary temperatures, while the fatty acids of other series (*e. g.*, oleic, linoleic, ricinoleic) are liquid, a more or less complete separation can be effected by subjecting the mixture to filtration or pressure. The latter plan is employed with considerable success on a large scale. Crystallisation from hot alcohol also serves to free the solid fatty acids from those fluid at ordinary temperatures, but neither plan allows of the latter being obtained even moderately free from admixed solid acids, and such methods are quite useless for quantitative work.

A general method by which stearic acid and its homologues may be separated from oleic and other liquid fatty acids, is based on the fact that the lead salts of the acids of the stearic series are almost insoluble in ether, while the corresponding compounds of the other fatty acids are soluble. Since the lead salts of the solid acids are not wholly insoluble in ether, and those of the drying fatty acids are not completely dissolved, the results are not strictly accurate. The best method of operating is probably that of Muter and De Koningh. 3 grm. of the fat should be treated, in a flask furnished with a long tube, with 50 c.c. of alcohol and a fragment of potassium hydroxide. The contents of the flask are boiled till hydrolysis is complete, when a drop of phenolphthaleïn solution is added and acetic acid until the solution is slightly acid. An alcoholic solution of potassium hydroxide is then added drop by drop until a faint permanent pink tint is obtained, when the liquid is slowly poured, with constant stirring, into a beaker containing a boiling solution of 3 grm. of neutral lead acetate in 200 c.c. of water. The solution is rapidly cooled and stirred at the same time, to induce agglomeration of the precipitate, and the clear liquid is poured off. The precipitate is well washed, by decantation, with boiling water and transferred to a stoppered bottle, in which it is treated with 120 c.c. of ether and allowed to remain 12 hours. (Wallenstein and Finck use a Drechsel gas-washing flask having the tube shortened about two-thirds to contain the ethereal solution, and pass a current of hydrogen through it for about a minute. In the case of colourless fats the liquid is said to remain practically colourless at the end of 12 hours, but if free access of air is permitted, a dark yellow solution is produced by oxidation.) Lead oleate, hypogeate, linoleate or ricinoleate will be dissolved by the ether, leaving lead laurate, myristate, palmitate, stearate, and arachidate undissolved. Lead erucate is sparingly soluble in cold ether, but readily in hot. The contents of the bottle are filtered through a covered filter into a Muter separating-tube (Fig. 12), 40 c.c. of dilute hydrochloric acid (1:4) added and the tube shaken till the clearing of the ethereal solution shows that the decomposition of the lead soaps is complete. The aqueous liquid, containing lead chloride and excess of hydrochloric acid, is run off through the bottom tap, water added, and agitated with the ether, and the process of washing by agitation repeated until the removal of the acid is complete. Water is then added to the zero mark and sufficient ether to bring the ether to a definite volume (*e. g.*, 200 c.c.). An aliquot portion of this (*e. g.*, 50 c.c.) is then removed through the side tap and the residual fatty acid weighed after evaporation of the ether in a current of coal-gas or carbon dioxide. Another aliquot portion of the ethereal solution should be distilled to a small bulk (avoiding complete evaporation of the ether), alcohol added and the solution titrated with N/10 potassium hydroxide and phenolphthaleïn, from which the fatty acids may be calculated from the result, or their mean combining weight deduced therefrom. A third aliquot part of the ethereal solution should be evaporated at about 60° in a flask traversed by a rapid stream of dry carbon dioxide. When every trace of ether is removed, 50 c.c. of Hübl's iodine solution should be added, the stopper inserted and the liquid kept in absolute darkness for 12 hours, after which an excess of potassium iodide solution is added and 250 c.c. of water, and the excess of iodine ascertained with thiosulphate solution in the usual way. From the result the iodine value of the liquid fatty acids is calculated, and an opinion may be formed respecting the proportions of oleic, linoleic, and other unsaturated acids present.

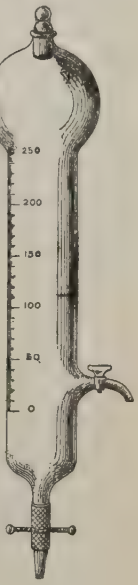

FIG. 12.

The table on the following page shows the results obtained with various fats and oils:

If it is desired to estimate *stearic acid and its homologues*, the lead soaps insoluble in ether should be detached from the filter and heated for some time with dilute hydrochloric acid, the liberated fatty acids being allowed to solidify, and then removed and weighed. The product may contain *arachidic*, *stearic*, *palmitic*, *myristic*, and *lauric acids*, besides the less commonly occurring acids of the same series. A modification of the method specially suited for the estimation of arachidic acid is described on page 93. If it is found impossible to remove the whole of the fatty acids from the filter, the latter should be treated with hot dilute hydrochloric acid, and then washed with a mixture of alcohol and ether, the fatty acids being recovered by evaporating the solution so obtained.

	Iodine number of		Observer
	Fat	Liquid fatty acids	
Lard, American	66.0	104.0 (highest)	v. Raumer.
Lard, American	65.4	104.5	Wallenstein and Finck.
Lard, Berlin	52.7	96.6	Wallenstein and Finck.
Lard, German		96.2 (highest)	v. Raumer.
Lard, Vienna	60.9	95.2	Wallenstein and Finck.
Lard, Hungarian	60.4	96.2	Wallenstein and Finck.
Lard, Roumanian	59.5	96.0	Wallenstein and Finck.
Lard		93.0 (highest)	Muter and DeKoningh.
Lard		94.0 (highest)	v. Asboth.
Beef tallow		90.0	Muter and DeKoningh.
Beef tallow, Australian	38.3	92.2	Wallenstein and Finck.
Beef tallow, Berlin	45.2	92.4	Wallenstein and Finck.
Beef tallow, Hungarian	38.6	92.7	Wallenstein and Finck.
Cottonseed oil		135.0	Muter and DeKoningh.
Cottonseed oil		136.0	v. Asboth.
Cottonseed oil, American, white	108.0	147.5	Wallenstein and Finck.
Cottonseed oil, American, yellow	107.8	147.3	Wallenstein and Finck.
Cottonseed oil, Egyptian	106.5	146.8	Wallenstein and Finck.
Cottonseed oil, Peruvian	106.8	147.8	Wallenstein and Finck.
Maize oil	122.0	140.7	Wallenstein and Finck.
Nigerseed oil	133.5	147.5	Wallenstein and Finck.
Arachis oil	98.9	128.5	Wallenstein and Finck.
Rape oil	101.1	120.5	Wallenstein and Finck.
Coconut oil	8.0	54.0	Wallenstein and Finck.

Lewkowitsch, however, recommends that the Muter tube be not used, the ethereal solution of the fatty acids being merely filtered through a folded filter into a flask. The ether is evaporated and the last traces of water are removed in a current of carbon dioxide by immersing the flask in boiling water.

The method is only approximately accurate and possesses the disadvantage, that the filtration of the ethereal solution is frequently slow and consequently oxidation can hardly be avoided. Other solvents have been proposed, notably petroleum ether b. p. below 80°, in which lead palmitate and stearate are much less soluble than in ether (Twitchell, *J. Soc. Chem. Ind.*, 1895, **14**, 516) and benzene (Fahrnsteiner, *Zeit. Unters. Nahr. Genussm*, 1898, 390), the lead salts of the fatty acids being insoluble in this medium at 8 to 12°. This method is, however, not so exact as the lead salt-ether method, and preference should be given to the latter.

Separation of the saturated acids from the unsaturated has also been proposed by means of sulphuric acid (Twitchell, *J. Soc. Chem. Ind.* 1897, **16**, 1002) and by means of the greater solubility of the lithium salts of the unsaturated acids in alcohol (Partheil and Ferie; *Arch. Pharm.*, 1903, **241**, 545), but these methods have been adversely criticised and appear to offer no advantages over the older method.

Hehner and Mitchell have devised the following method of the estimation of *stearic acid:* Prepare a supply of alcohol saturated at 0° with pure stearic acid or with stearic acid which only contains traces of palmitic acid. Dissolve from 0.5 to 1 grm. of the mixture of fatty acids to be examined if these are solid, or about 5 grm. if fluid, in about 100 c.c. (exact measurement is not necessary) of the stearic alcohol solution. Leave this liquid in an ice-bath overnight, agitate the mixture next morning and allow to stand in ice for a short time; filter off while the mixture remains in ice, wash with stearic alcohol solution at 0°, dry and weigh. Ascertain the m. p. of the product which should not be much less than 68.5°. Since the sides of the interior of the flask, as well as the residue of crystallised stearic acid retain a small amount of the alcoholic solution, a correction experimentally found to be 0.005 grm. has to be applied, this amount being deducted from the total weight found. In their experiments the authors used methylated alcohol of sp. gr. 0.8183, but obviously the exact strength is a matter of no consequence.

For maintaining a constant temperature, Hehner and Mitchell used an ice-chest consisting of a metal box with sockets soldered to its sides to receive clamps for holding flasks, submerged to the neck in ice-water, in which the analyses were carried out. The metal box was fitted in a wooden box, and the space between the metal and wood was packed with wool and sawdust, while a cushion of wool and flannel was placed between the lids of the metal and wooden boxes.

For the preparation of the stearic solution about 3 grm. of pure stearic acid were dissolved in about a litre of warm alcohol of sp. gr. 0.8183, and the stoppered bottle containing the solution placed overnight in the ice-water (which contained lumps of ice) in the chest, so that the bottle was submerged up to the neck. After 12 hours a considerable portion of the stearic acid had crystallised out. The saturated mother-liquor was syphoned off without removing the bottle from the ice-water. The filtering syphon consisted of a small thistle funnel twice bent at right angles, fitting with its straight limb into a flask in connection with a suction pump. The bulb of the funnel, which was submerged in the ice-cold solution, was covered over with a piece of fine calico. On applying suction, a perfectly clear stearic solution was obtained, saturated at 0°, or rather at 0.2°, which was the temperature almost constantly shown by a standard thermometer.

A precisely similar mode of filtration was also adopted in the quantitative experiments on mixed fatty acids, the thistle funnel used being a miniature one, with a bulb not larger than about 0.25 of an inch in diameter.

ESTIMATION OF STEARIC ACID IN MISCELLANEOUS FATS.

	Taken grm.	Iodine number	Stearic acid 0.005 grm.	Percentage in fatty acids
Beef stearine	0.3024	2.0	0.1516	50.19
Beef stearine	0.4174	....	0.2131	51.05
Oleomargarine	1.0107	46.50	0.2295	22
Oleomargarine	0.5192	....	0.1104	21.26
Oleomargarine	1.1100	....	0.2630	23.6
Margarine I	1.0035	....	0.2495	24.8
Margarine II	0.5000	41.19	0.0586	11.72
Horse-kidney fat	0.701	85.4	no deposit	.....
Cotton oil "stearine"	0.9945	....	0.0334	3.3
Stillingia tallow	....	22.87	no deposit	.....
Cacao butter	1.0168	....	0.3878	40.6
Cacao butter	0.9548	....	no deposit	.....
Maize oil	5.4186	122	no deposit	.....
Almond oil	5.0236	95.68	no deposit	.....
Olive oil	5.5558	....	no deposit	.....
Earthnut oil	1.0648	....	0.0751 (m. p. 67°)	7.0

Numerous estimations of the stearic acid in butter were made. In many cases none, or a minute quantity only, was found. In some cases phenomena of supersaturation apparently occurred. On the first examination in the morning the solution was perfectly clear, but after shaking the contents and allowing to stand some time longer in the ice, a small but increasing quantity of crystals formed.

The method appears to be inapplicable to the fatty acids from Japan wax. From mixtures of these with pure stearic acid, the latter could only be recovered partially, and in some cases not at all.

Kreis and Hafner (*Zeit. Nahr. Genussm.*, 1903, **6**, 22) state that this method gives trustworthy results provided that not less than 0.5 grm. of the mixed fatty acids is taken, as stearic acid easily forms supersaturated solutions. This is borne out by Emerson (*J. Am. Chem. Soc.*, 1907, **29**, 1750) and is said to explain the differences in the solubility obtained. Appended are results:

Hehner and Mitchell found solubility at 0° in 94.4% alcohol 0.15 grm.

Kreis and Hafner found solubility at 0° in 95% ethyl alcohol 0.1249 grm.

Emerson found solubility at 0° in 95% ethyl alcohol 0.1123 grm.

The alcohol used by Hehner and Mitchell, as already pointed out, was rectified methylated spirit.

Other methods of separating oleic from stearic acid or of estimating the former in mixtures of the two are described on page 407. A method for separating oleic from palmitic acid is also described on page 407.

Separation of Fatty Acids from Resin Acids.—As already pointed out, Twitchell's method has been found to be the most satisfactory (see page 77).

Separation of Fatty Acids from Soaps, Hydrocarbon Oils, etc.—The estimation of the constituents of complex mixtures of fatty acids with neutral oils, hydrocarbons, etc., has already been described (see table on page 83). Small quantities of neutral fats contained in free fatty acids may be detected by dissolving the substance in hot alcohol and adding a few drops of strong ammonia to the solution; in the presence of mere traces of neutral fat, the solution is rendered turbid.

PALMITIC ACID.

$C_{16}H_{32}O_2 = C_{15}H_{31}COOH.$

The glyceride of palmitic acid occurs largely in palm oil, Chinese tallow, the fat of coffee-beans, coconut oil, butter-fat, tallow, and lard. Palmitic esters of monatomic radicals exist in spermaceti, beeswax, and opium wax.

Palmitic acid is conveniently prepared from palm oil, which should be saponified with potassium hydroxide, the solution of the resultant soap decomposed by dilute sulphuric or hydrochloric acid, and the liberated fatty acid purified from the accompanying oleic acid by repeated crystallisation from hot alcohol, till the pressed crystals have m. p. 62°. Chittenden and Smith prepare palmitic acid from myrtle wax, which is said to contain only lauric acid in addition. By repeatedly crystallising the separated fatty acids from hot alcohol, pure palmitic acid, melting at 62°, is readily obtained. Palmitic acid is manufactured on a large scale by the action of potassium hydroxide upon oleic acid at a high temperature, or by saponifying palm oil and pressing the fatty acids obtained. The product is commonly, but improperly, called "palmitine."

Palmitic acid is a white substance, melting at 62.62° (de Visser) to a colourless oil, which solidifies on cooling to a white, finely crystalline mass. It is insoluble in water or dilute acids, but is soluble in alcohol, ether, carbon disulphide, hydrocarbons, and fixed oils. It cannot be distilled without decomposition under ordinary pressure, even in the absence of air; but distils, practically unchanged, at 271.5°/100 mm.

Palmitic acid is but slightly soluble in cold alcohol. Hehner and Mitchell (*Analyst*, 1896, **21**, 323) have found 100 c.c. of methylated alcohol (94.4% by volume) to dissolve the following quantities after being kept at 0° for the time stated.

No. of hours	Grm. dissolved	No. of hours	Grm. dissolved
12	1.298–1.320	108	1.086
36	1.244	132	1.044
60	1.211	156	1.028
84	1.134		

Kreis and Hafner (*Ber.*, 1903, **36**, 2769) found 95% alcohol to dissolve at 0° 0.56 gram.

The hot alcoholic solution has an acid indication, and on cooling deposits the acid in tufts of small white needles.

Crystallisation from hot alcohol may be employed to separate palmitic acid from *oleic acid*, and, if repeated sufficiently often, from its lower homologues *myristic* and *lauric acids*. Mixtures of palmitic acid with certain proportions of myristic or lauric acid are, however, said to be incapable of analysis by fractional crystallisation from alcohol or ether. Mixtures of these homologous acids in certain proportions melt at a lower temperature than either acid separately. The method of ascertaining the composition of such mixtures, including those containing *stearic acid*, is described on page 383 *et seq*.

A method of separating palmitic acid from *oleic* and *linoleic acids* and their homologues is given on page 386. A method of separating palmitic and oleic acids, which is useful for analysing the product obtained by saponifying palm oil by the autoclave process, is described on page 406. Commercial palmitic acid may be examined in the same manner as stearic acid.

Chittenden and Smith (*Amer. Chem. J.*, 1885, **6**, 217) find that the presence of free acetic acid increases the solubility of barium, magnesium, and lead palmitates in alcohol to such an extent as to render the separation of the acid in these forms incomplete. Further, the precipitates undergo partial decomposition when washed, either with water or with alcohol containing acetic acid.

Metallic Palmitates.—These present the closest resemblance to the corresponding stearates (page 399 *et seq.*), and require but little separate description. Barium, magnesium, and lead palmitates are more readily soluble in alcohol, especially in presence of acetic acid than are the corresponding stearates.

Adipocere, a wax-like substance found in large quantity in corpses buried under certain conditions, is said to consist largely of palmitic acid mixed with potassium and calcium palmitates.

Aluminium palmitate may be prepared in a manner similar to the corresponding oleate. It is an elastic amorphous mass, insoluble in water, but dissolving in petroleum spirit and oil of turpentine to form very viscid solutions which have found applications as varnishes. The film of aluminium soap left on evaporation retains its elasticity, and is odourless and impervious to water (see *J. Soc. Chem. Ind.*, 1882, **1**, 278). Aluminium palmitate has some practical interest as an ingredient of "oil pulp" or "thickener."

Palmitic Esters.—These present a close analogy to the corresponding stearates.

Glyceryl Palmitates or Palmitins are obtainable synthetically by means similar to those employed for the preparation of the stearins. Chittenden and Smith (*Amer. Chem. J.*, 1885, **6**, 217) have given the following data:

	α-Monopalmitin	α-Dipalmitin	Palmitin
100 parts of absolute alcohol, at 20–21°, dissolve,	4.135	0.210	0.005
Appearance of fat deposited from alcoholic solution,	Small spherules, showing no distinct crystalline form.	Long curved needles.	Groups of irregular crystals.
Appeaance of fat deposited from ethereal solution,	Rhombic plates, either single or in branches.	Warty masses.	Irregular doubly curved bodies, single and crossed in groups.
M. p.	53.0°[1]	61.0°[2]	62–64°[3]
Solidifying-point	62.5°	57.0°	45.5–47°

[1] Krafft (*Ber.*, 1903, **36**, 4343) gives m. p. 72°.

[2] Probably a monoglyceride; Grün (*Ber.*, 1905, **38**, 2284) m. p. 70°.

[3] Scheij (*Rec. Trav. Chim.*, 1899, **18**, 169) gives m. p. 65.1°, sp. gr. 0. 8657/80°; Guth (*Zeit. Biol.*, 1902, **44**, 78), m. p. 65.5°.

An isomeric modification of dipalmitin, the β, has been obtained, m. p. 67.2°. There was also obtained a very stable mixture of 1 part of palmitin with 3 of dipalmitin. This product crystallised from alcohol in bunches of needles, which melted at 68° to 69° and solidified between 64° and 67°.

STEARIC ACID.

$$C_{18}H_{36}O_2 = C_{17}H_{35}COOH.$$

The glyceryl ester of this acid occurs extensively in nature, especially in the harder fats of the animal kingdom, such as mutton and beef suet.

Pure stearic acid may be prepared by hydrolysing tallow with potassium hydroxide, decomposing the solution of the resultant soap with a dilute acid, and purifying the liberated fatty acids from oleic acid by crystallisation from hot alcohol. The pressed crystals consist essentially of a mixture of stearic and palmitic acids. It should be purified by recrystallisation, and 4 parts dissolved in such a proportion of hot alcohol that nothing will separate out on cooling to 0°. A solution of 1 part magnesium acetate in boiling alcohol is added and the liquid allowed to cool, when magnesium stearate will separate (page 384). The precipitate is filtered off, washed with cold alcohol, boiled with water and hydrochloric acid, and the purity of the resultant stearic acid proved by a careful determination of the m. p. which should be 69.32° (de Visser).

The commercial product commonly termed "stearine" really consists of a mixture of free stearic and palmitic acids, and may be conveniently employed for the preparation of pure stearic acid, instead of tallow or other fat. The "stearine" may be at once dissolved in hot alcohol and the solution precipitated with magnesium acetate as above described. Commercial stearine often contains a considerable admixture of paraffin wax or other hydrocarbons, the absence of which should be proved before employing the substance for the preparation of stearic acid.

Shea-butter, when obtainable, may be conveniently employed as a source of stearic acid, as the fatty acids produced by its hydrolysis consists solely of stearic and oleic acids, which can be separated perfectly by repeated crystallisation from hot alcohol.

Stearic acid presents the closest resemblance to palmitic acid, the following being the most tangible distinctions:

	Palmitic acid	Stearic acid
M. p.	62.62°	69.32°
B. p./100 mm.	271.5°	287°
Solubility in cold absolute alcohol	9.3%	2.5%
Manner of crystallisation from alcohol	Tufts of small white needles.	Nacreous laminæ, or needles.
Behaviour with magnesium acetate	See page 384.	See page 384.
M. p. of lead soap	108°–112°	125°

In the analysis of natural oils and fats, the palmitic and stearic acids are usually obtained together, the oleic acid being separated by treating the lead soaps with ether, as described on page 390. In the mixture of palmitic and stearic acids thus obtained, the proportions of the two constituents can be approximately ascertained by one of the methods described on page 381 *et seq.*, but the rigidly accurate analysis of such mixtures is not at present possible.

Commercial stearic acid differs much in quality and appearance according to its source, but usually consists of a mixture of stearic acid with more or less palmitic and, sometimes, oleic acid. Hydrocarbons and unsaponified fat may also be present, but the proportion of these impurities is seldom large. The method of assay is similar to that employed for oleic acid, with the addition of ascertaining the solidifying point by the "titer test," from which the relative proportions of stearic and palmitic acids in the sample can be deduced; or, in the absence of hydrocarbons and unsaponified oil, the proportions of stearic and palmitic acids can be deduced from the results of the titration with standard alkali (page 383). The proportion of oleic acid may be ascertained by multiplying the iodine-absorption by 1.11 (page 378).

Metallic Stearates.—Stearic acid forms a well-defined class of salts, all of which, with the exception of those of the alkali-metals, are insoluble in water, and mostly in alcohol and ether.

The stearates present very close resemblances to the palmitates, the chief tangible points of distinction being the more ready solubility of magnesium palmitate in alcohol and the different m. p. of the lead salts. Lead palmitate melts at 108°, according to Maskelyne, and between 110° and 112°, according to Heintz, while lead stearate melts at

125°. Palmitates and stearates may also be distinguished by the m. p. and combining weights of the liberated fatty acids.

Potassium stearate may be prepared by saturating a hot alcoholic solution of stearic acid with alcoholic potassium hydroxide, using phenolphthaleïn as indicator. On concentrating the solution and allowing it to cool, the potassium stearate crystallises in shining needles or laminæ. It also separates on cooling a solution of 1 part of stearic acid and 1 of potassium hydroxide in 10 parts of water. The opaque granules formed may be purified by crystallisation from alcohol. Or a boiling alcoholic solution of stearic acid may be mixed with an excess of a boiling aqueous solution of potassium carbonate, the liquid evaporated to dryness, the residue extracted with boiling alcohol, and the filtered solution allowed to cool, when crystals of potassium stearate will be deposited.

Potassium stearate dissolves in about 10 times its weight of water at the ordinary temperature, forming a mucilaginous mass. On heating the solution it becomes clear, and if diluted with a large proportion of cold water *hydrogen stearate* of the composition $KH(C_{18}H_{35}O_2)_2$ separates in delicate, white, pearly laminæ, while a basic stearate remains in solution. An analogous decomposition by excess of water is suffered by other alkali-metal salts of the higher fatty acids, and is a leading cause of their application as soaps.

Ammonium stearate is obtained as a crystalline mass by incorporating strong ammonia with melted stearic acid, and keeping the product over sulphuric acid till the excess of ammonia has evaporated. On further keeping in this manner, it gradually loses ammonia. (Wright and Thompson.)

Sodium stearate resembles the potassium salt, but is harder. It is decomposed in a similar manner, but with greater facility, by excess of water, and is less soluble in alcohol than potassium stearate. Sodium stearate may be separated from sodium palmitate by fractional crystallisation from hot alcohol.

Barium and calcium stearates are crystalline precipitates insoluble in water. The *magnesium* salt is similar, but soluble in boiling alcohol.

Lead stearate, as prepared by double decomposition, forms a white amorphous powder, melting at 125° to a colourless liquid, which solidifies on cooling to an opaque amorphous mass. It is insoluble in water, alcohol, ether, or petroleum spirit. In these characters it is simulated by lead palmitate, myristate, arachidate, etc., but the lead salts of oleic acid and its homologues, as also of linoleic and ricinoleic acids, are soluble in ether and petroleum spirit.

Stearic Esters.—*Ethyl stearate* is prepared by passing hydrogen chloride into a solution of stearic acid, in absolute alcohol. It is also formed by boiling tristearin with sodium oxide, or with a quantity of alcoholic potassium hydroxide insufficient for its complete saponification. Ethyl stearate is a crystalline, easily fusible, wax-like solid, m. p. 33.7°, readily soluble in alcohol and ether, and b. p. 224° with partial decomposition, b. p. in a vacuum 139° or 154° (Krafft).

Glyceryl stearates are obtainable synthetically by heating together, under pressure, suitable proportions of stearic acid and glycerol. Products containing either 1, 2, or 3 molecules of the stearic radicle are thus obtainable. Another method of obtaining stearin consists in testing $\alpha\beta\gamma$-tribromopropane and sodium stearate at 170–180° for ten hours.

Monostearin and distearin do not appear to occur naturally, but *glyceryl stearate* is identical with the stearin which, in admixture with palmitin, constitutes the less fusible portion of solid fats. For brevity, this stearate is frequently called "stearin." It is not identical with commercial "stearine," which is a mixture of free stearic and palmitic acids obtained by the saponification of the neutral fats.

Stearin forms white, shining nodules, fine needles, or pearly laminæ resembling spermaceti. It is tasteless, neutral, and volatile almost without decomposition in a vacuum. Heated to a high temperature, it decomposes and gives off acrolein. It appears to exist in two isomeric modifications. As crystallised from ether it has a m. p. of 71.6°, sp. gr. 0.8848/60° (Scheij, *loc. cit.*). If the crystals so obtained be heated 4° or more above the m. p., they are converted into a modification which solidifies to a waxy mass at 52°, and melts at 55°. If the latter be reheated a few degrees above the m. p., the original substance, melting at 71.6°, is obtained (Guth, *loc. cit.*).

Stearin is insoluble in water and nearly insoluble in rectified spirit. In boiling absolute alcohol it dissolves freely, and is deposited in flocks on cooling. Stearin also dissolves readily in boiling ether, but the liquid retains less than 0.5% on cooling. It is readily soluble in fixed and volatile oils, and in carbon disulphide. When heated in a vacuum, it distils almost unchanged, but under the ordinary pressure it is decomposed with formation of carbon dioxide, acetic acid, water, free carbon, and olefines of b. p. ranging from 190 to 245°.

Pure stearin does not change on exposure to air at the ordinary temperature. When impure, it is liable to become rancid, apparently owing to the presence of olein. Stearin readily undergoes saponification when heated with alkalis or other strong bases, with formation of a metallic stearate and glycerol.

OLEIC ACID.

$C_{18}H_{34}O_2$.

Oleic acid is one of the most widely distributed fatty acids, occurring as an ester in most non-drying fixed oils, especially almond and olive oils, and in smaller proportion also in solid fats, such as lard, palm oil, butter, and goose fat.

For the preparation of pure oleic acid an oil rich in olein, as almond or olive oil, is saponified by alkali, the soap dissolved in water and decomposed by excess of dilute hydrochloric or sulphuric acid. White Castile soap may be employed as the starting-point, thus saving the trouble of saponifying. The use of commercial oleic acid is not to be recommended, owing to the frequent presence of hydrocarbons. The liberated fatty acids are separated from the aqueous liquid, and heated for some time on the water-bath with about 1 part of finely ground lead monoxide for every 20 parts of oil taken for the operation. Excess of lead oxide should be avoided, as it occasions the formation of a basic oleate, which is subsequently treated with difficulty. The proportion of lead oxide prescribed is insufficient to combine with all the fatty acid, but the result is merely that a portion of the oleic acid remains in the free state, while the more powerful palmitic and stearic acids form lead salts.

The product is next treated with about twice its volume of ether, which dissolves the lead oleate and free oleic acid, and leaves the lead palmitate and stearate unchanged. The solution is separated from the insoluble salts, and hydrochloric acid added until the aqueous liquid has a strongly acid indication even after shaking. The lower layer now contains lead chloride, while the ether retains the oleic acid. It is separated from the acid liquid, washed by agitation with water, and the ethereal layer removed and the ether evaporated off as rapidly and at as low a temperature as possible.

According to E. C. Saunders, rectified spirit (sp. gr. 0.82) may be advantageously substituted for the ether prescribed in the above process.

The oleic acid obtained by the foregoing process is apt to retain a little colouring matter and products of oxidation. To remove these, Bromeis recommends that it should be cooled below its solidifying-point, and subjected to strong pressure between folds of filter-paper. The residual oleic acid is melted, again cooled, and the purification by pressure repeated. Another method of purification consists in dissolving the oleic acid in ammonia, precipitating the solution by barium chloride, purifying the barium oleate by crystallisation from alcohol, and then decomposing it with tartaric or other suitable acid.

Pure oleic acid is a colourless, odourless, tasteless oily liquid, having sp. gr. 0.900 at 11.8°, 0.897 at 19°, and 0.876 at 100°. When cooled to about 4°, it solidifies to a white crystalline mass, and on cooling its hot alcoholic solution is deposited in white needles, m. p. 14°. Its purity should be tested by means of the iodine value—the pure acid has an iodine value 90.

Pure oleic acid is not altered by exposure and is neutral, but the impure substance gradually absorbs oxygen, becomes yellow, and acquires an acid indication and a rancid taste and smell. The altered product has a lower m. p. than the pure acid. Oleic acid is much thinner than the neutral fixed oils, and is less liable to leave a greasy stain. When applied to the skin it wets it almost like water, and is very rapidly absorbed.

Oleic acid is insoluble in water, but dissolves with facility in alcohol, ether, carbon disulphide, chloroform, and hydrocarbons, and is also miscible with neutral fats and essential oils. The solution of oleic acid in alcohol usually has an acid reaction to litmus, a fact said to be due to the presence of impurities. It turns milky when largely diluted with spirit, but the turbidity disappears on adding a few drops of hydrochloric acid. Oleic acid dissolves in ammonia and solutions of alkalies to form oleates, from which others may be obtained by double decomposition.

Oleic acid may be distilled in a vacuum or in a current of superheated steam at 250° without material alteration; but if distilled in contact with air it is partially decomposed, with formation of carbon dioxide, hydrocarbons, acetic, caproic, caprylic, capric, sebacic, and other acids. It has b. p. 153°/0 mm., 264°/50 mm., 285.5°/100 mm.

Sebacic acid, $C_8H_{16}(COOH)_2$, is also produced when oleic acid is *rapidly* heated with excess of alkali. Its formation is a characteristic test for oleic acid and its immediate homologues. To detect it the alkaline residue should be treated with boiling water, and the liquid acidified with acetic acid, again boiled, and filtered hot. The filtered liquid will, on cooling, deposit brilliant needles of sebacic acid, m. p. 127°, and soluble in 1000 parts of cold or 50 of boiling water.

When more strongly heated with potassium hydroxide, oleic acid yields potassium palmitate, oxalate and acetate, and free hydrogen, secondary products being also formed. The temperature necessary for this change is 300° to 320°. The process is commercially employed for the production of palmitic acid. The following formula expresses the main change which occurs:

$$C_{18}H_{34}O_2+2KHO=KC_{16}H_{31}O_2+KC_2H_3O_2+H_2.$$

Small quantities of sebacic acid, caproic acid, caprylic alcohol and other compounds are also produced. The details of this process of manufacturing palmitic acid, for which nearly all fatty substances, except mare's grease and suint fat, are available, have been described by W. Lant Carpenter (*J. Soc. Chem. Ind.*, 1883, **2**, 98. Compare also Lewkowitsch, *J. Soc. Chem. Ind.*, 1879, **16**, 390).

Oleic acid combines with a molecule of bromine to form dibromo-stearic acid, $C_{18}H_{34}O_2,Br_2$ as a yellow viscous oil having a fruit-like odour. Oleic acid also combines in a perfectly definite manner with Hübl's reagent, and may be estimated by that means.

Oleic acid is dissolved by concentrated sulphuric acid, a conjugate acid being formed which has been used in Turkey-red dyeing and calico-printing.

Strong nitric acid oxidises oleic acid, acids of the acetic and oxalic series (including succinic acid) being formed.

By oxidation with potassium permanganate in presence of an excess of potassium hydroxide, oleic acid yields dihydroxystearic acid, a crystalline compound, m. p. 131.5 to 132°, and solidifying at 119° to 122°. For details of preparation consult Le Sueur (*Trans. Chem. Soc.*, 1901, **79**, 1315).

When oleic acid is heated to 200° or 210° in a sealed tube with amorphous phosphorus and fuming hydriodic acid, it assimilates hydrogen, and is converted into stearic acid.

When the red fumes generated by acting on nitric acid by starch or arsenious oxide, or by a mixture of sulphuric acid and sodium nitrite, are passed for a short time into oleic acid carefully kept cold, the liquid gradually thickens, and in the course of an hour or so solidifies to a crystalline mass of an isomer of oleic acid called elaïdic acid. It may be purified by agitation with boiling water, followed by crystallisation from alcohol.

Elaidic acid, $C_{18}H_{34}O_2$, forms large pearly plates, resembling benzoic acid, m. p. 51–52°, and distilling almost unchanged. B. p. 154°/0 mm., 266°/50 mm., 287.8°/100 mm. In the solid condition it is unchanged in the air, but in the fused state it readily absorbs oxygen, becoming yellow and pasty, and acquiring an odour like that of poppy oil. With bromine, fused potassium hydroxide, and phosphorus and hydriodic acid, elaïdic acid behaves like oleic acid. Elaïdic acid has a strong acid reaction, and forms a series of well-defined salts, all of which, if neutral, are said to be insoluble in water. *Sodium elaïdate* crystallises from alcohol in silvery laminæ, and the *potassium* salt in glistening needles. The *barium* and *lead* salts are white precipitates.

The property of forming an isomer of higher m. p. under the influence of nitrous acid is not peculiar to oleic acid. It is exhibited also by its olein, by its homologues hypogeic, deglic, and erucic acids, by ricinoleic acid, but not by the fatty acids characteristic of the drying oils.

Estimation of Oleic Acid.—When occurring in the free state and unmixed with other acids, oleic acid may be conveniently and accurately estimated by titration with standard alkali (page 9). In presence of acids of the stearic series it may be titrated with Hübl's solution, each c.c. of N/10 iodine absorbed corresponding to 0.0141 grm. of oleic acid. The estimation of oleic in presence of linoleic acid is described on page 378.

Oleic acid may be estimated gravimetrically when in admixture with acids of the stearic series by utilising the solubility of its lead salt in alcohol, ether, or petroleum spirit, in the manner described for its preparation (page 402). The best method of applying the principle for analytical purposes is described on page 390.

According to F. Sear, palmitic and oleic acids can be separated by heating the mixture with excess of zinc oxide and digesting the product in the cold with carbon disulphide.

David's method for estimating oleic acid in the presence of stearic acid, described in the third edition of this work, is inaccurate.

A method for the approximate estimation of oleic and solid fatty acids in tallow is described on page 213.

Commercial Oleic Acid.—Commercial oleic acid is obtained by subjecting to hydraulic pressure the mixture of fatty acids produced by the hydrolysis of tallow, palm oil, and similar fats. The expressed liquid, technically known as "red oil," contains a considerable quantity of palmitic and stearic acids, which separate out on keeping the red oil for some time at a low temperature.

When fats are hydrolysed by the autoclave process, the products often contain a considerable proportion of unchanged fats. In consequence of the comparative facility with which palmitin and stearin are hydrolysed, the unaltered fat consists chiefly or wholly of olein, which, owing to its low m. p., becomes concentrated in the oleic acid expressed from the crude product. Hydrolysis under high pressure always tends to cause more or less decomposition of the higher fatty acids, and, when actual distillation has been resorted to, notable quantities of acetic, suberic, and sebacic acids are formed, and the two latter will remain with the oleic acid, together with certain hydrocarbons, apparently belonging to the paraffin series, which are always simultaneously produced.

Commercial oleic acid, which is frequently, but improperly, called "oleine," varies considerably in properties and composition. It is sometimes a clear liquid, ranging in colour from dark brown to pale sherry, while other specimens are quite pasty from separated solid fatty acids. By distillation in a current of steam, oleic acid may be obtained wholly free from colour, but possessing an acrid odour from the presence of decomposition-products. Undistilled oleic acid usually retains an odour suggestive of its origin. The sp. gr. is also variable, ranging from about 0.887 to 0.908, or even more, according to the proportions of hydrocarbons, neutral oils, and solid fatty acids which happen to be present.

Mineral acids are sometimes present in sensible quantity in commercial oleic acid. They rarely interfere with its applications; but, if necessary, may be detected and estimated as on page 75, or by titrating the alcoholic solution with alkali and methyl-orange.

The presence of an abnormal proportion of *oxidation* and *secondary products* of an acid character is indicated by agitating 50 c.c. of the oleic acid with 1 c.c. of a 10% solution of ammonia and 50 c.c. of water. Both the oleic acid and the aqueous liquid should by this means be deprived of any acid reaction of litmus.

The presence of *palmitic* or *stearic acid* in commercial oleic acid may be detected by saponifying the sample with alcoholic potassium hydroxide, adding a drop of phenolphthaleïn solution, and then acetic acid, drop by drop, until the pink colour is just destroyed. The liquid is then filtered, mixed with twice its weight of ether, and an alcoholic solution of lead acetate added. Any white precipitate may consist of stearate or palmitate of lead, and may be filtered off, washed with ether, decomposed with dilute hydrochloric acid, and the liberated fatty acids weighed. All ordinary commercial oleic acid will indicate the presence of foreign fatty acids when examined in this manner.

Neutral fats will be indicated by the gradual separation of oily drops when equal volumes of the sample and of alcohol are heated at 25° for some time, while a pure acid will give a clear solution when thus treated. A very delicate test for neutral fats in oleic acid is described on page 395.

The presence of neutral fixed oils or hydrocarbon oils can also be inferred from the diminished proportion of alkali required, when the sample is titrated as on page 9. 5 grm. of pure oleic acid will require 35.47 c.c. of $N/2$ potassium hydroxide, corresponding to 19.9% of KOH, and a combining weight of 282. Hence the percentage of *oleic acid* in the sample may be found by dividing the percentage of KOH required by 0.199. Any admixture of palmitic acid will *increase* the amount of alkali required.

The neutralised liquid resulting from the last process may be treated with a known amount of standard alcoholic potassium hydroxide, and examined by Köttstorfer's process, when each 1 c.c. of additional $N/2$ alkali neutralised will indicate the presence of 0.145 grm. of *neutral fixed oil* in the sample.

The liquid left after the second titration may be evaporated with a further quantity of alcoholic potassium hydroxide, the residual soap dissolved in water, and the solution agitated with ether, as described on page 79. The ethereal solution is then separated and evaporated, and the *unsaponifiable matter weighed.*

In the case of an oleic acid obtained by distillation of an ordinary fat with superheated steam, the unsaponifiable matter or ether-residue obtained in the last process consists of *hydrocarbons* presenting the closest resemblance to those contained in the lubricating oils manufactured from petroleum and bituminous shale. Hence no means exist at present by which an intentional addition of a moderate proportion of hydrocarbon oil to oleic acid can be positively detected.

According to Allen—the hydrocarbons normally present in distilled oleic acid range from 3 to 7%; and therefore any proportion notably in excess of the latter figure may be attributed to an intentional sophistication of the product with mineral or shale oil. The addition of these adulterants to oleic acid is extensively practised, although their presence greatly reduces the suitability of the oleic acid for one of its most important applications, which is that of greasing wool during the process of spinning. Any admixture of hydrocarbons reduces the property of ready saponifiability for which oleic acid is chiefly valued.

The foregoing statement respecting the proportion of unsaponifiable matter present in distilled oleic acid applies to a product obtained by saponifying pure substances. Wool grease and the grease obtained by treating with acid the soapy liquors in which wool has been washed are much more impure articles. Besides the *hydrocarbons* formed on distilling such greases, the distilled product is liable to contain *actual* petroleum or shale products used in the wool-spinning, either intentionally or as adulterants of other oils, *petroleum* employed for antiseptic purposes on the living sheep, and *cholesterol* and other unsaponifiable matters contained in the "suint" or wool fat. Hence, an estimation of the "unsaponifiable matter" in such low-class oleic acids cannot be regarded as a reliable indication of the extent to which they have been adulterated by an actual addition of hydrocarbon oil. Some indication of the origin of the unsaponifiable matter may be obtained by treating the ether-residue with thrice its volume of rectified spirit, when the volume left undissolved may be regarded as indicating roughly the hydrocarbons present, while the cholesterol and solid alcohols from sperm or bottlenose oil pass into solution. (See "Wool Fat.")

The following table are results obtained by Allen from an examination of specimens of commercial oleic acid of very different qualities. The "free fatty acids" were estimated by titration with standard alkali, and calculated to their equivalent of oleic acid; but in the case of the semi-solid samples containing much palmitic acid the result thus obtained is necessarily in excess of the truth. The percentage of ether-residue shows the "hydrocarbons, etc.," in the samples, while the esters were in some cases determined indirectly, in other cases calculated from the result of Köttstorfer's saponification process, and in others deduced from the difference between the free fatty acids of the original sample and the total fatty resulting from its saponification. The samples and ether-residues to which an *f* is affixed were noted as being distinctly fluorescent:

	A	B	C	D	E	F	G	H	I
Condition......	Clear	Clear	Fluid, with slight deposit	Semi-solid	Semi-solid	Contained much solid	......	Fluid	Clear
Colour.........	Pale brown	Pale brown *f*	Brown	Brown	Pale brown	Pale brown *f*.	......	......	Sherry brown *f*.
Sp. gr.	0.8996	......	0.9055	0.9085	0.9014	0.8987	......	0.8894	0.9083
Free fatty acids	96.3	93.8*f*.	80.3	83.7	96.2	84.5	89.4	77.2	55.3
Hydrocarbons, etc.	1.3	3.9*f*.	2.2	2.9	4.8*f*.	10.3	2.0	26.8	35.9*f*.
Esters, direct ..	......	......	....	13.4	......	3.3	......	......	11.6
Esters, by difference	2.5	2.3	17.5	17.0	......	2.0	8.6	4.0	8.8

The first 4 samples were manufactured by the autoclave process, A and C being derived from tallow. E and F were probably autoclave products, the latter being of French manufacture. G was obtained from tallow by lime-saponification, and H and I were probably distilled oleins from recovered grease.

Granval and Valser (*J. Pharm. Chim.*, [5], 1889, **19**, 232) have drawn attention to the fact that commercial oleic acid is sometimes adulterated with the acids from linseed oil. Such samples have a sp. gr. of from 0.912 to 0.919 and do not dissolve completely in nine volumes of rectified spirit. Shaken with an equal volume of sodium hydroxide solution, the mixture turns intensely yellow; pure oleic acid becomes grey. If the linseed-oil acids be present in considerable proportion, they may be detected by the high iodine number. Hazura (*J. Soc. Chem. Ind.*, 1889, **8**, 641) adopts the following method: 50 grm. of the sample are saponified on the water-bath with dilute alcoholic potassium hydroxide. The potash soap is freed from alcohol and dissolved in 1,000 c.c. of water. This strong alkaline solution is gradually mixed with 1,000 c.c. of a 5% solution of potassium permanganate. After 1/2 to 1 hour, the manganese oxide is filtered off, the filtrate acidified with sulphuric acid, and again filtered. The filtrate thus obtained is neutralised with potassium hydroxide, concentrated to about 300 c.c., and again acidified with sulphuric acid, which produces a precipitate. The acid liquid, without removing the precipitate, is shaken with ether. If the precipitate dissolves in ether, it consists of azelaic acid ($C_7H_{14}(COOH)_2$)

and the original oleic acid is free from linseed-oil acids. If it does not dissolve, it is filtered off, recrystallised several times from water or alcohol, with the addition of animal charcoal, and, after air-drying, its m. p. determined. If this be above 160°, linseed-oil acids are undoubtedly present.

Sulpholeic Acid.—When a non-drying fixed oil is cautiously treated with strong sulphuric acid, complex changes occur, the precise nature of which depends on the conditions of the experiment. P. Juillard (*J. Soc. Chem. Ind.*, 1894, **13**, 820) states that olein treated in the cold with sulphuric acid yields two acids—one monobasic, the other dibasic—which appear to be addition products of sulphuric acid and olein. They are soluble in water. Oleic acid treated with sulphuric acid produces at first hydroxystearo-sulphuric acid, $C_{17}H_{34}(OSO_2H)$-CO_2H, from which is formed hydroxystearic acid, $C_{17}H_{34}(OH)CO_2H$.

Metallic Oleates.—These form a well-defined series of salts, many of which have received practical applications. They may be obtained by dissolving the metallic oxide of which the oleate is required in warm oleic acid; but such a method does not give compounds of very definite composition. A preferable plan is to precipitate an aqueous solution of sodium oleate with a neutral solution of the salt of the metal of which the oleate is required. Zinc, aluminium, iron, lead, copper, bismuth, and other oleates are readily obtained in this way.

These oleates are readily analysed by agitating them with ether and a dilute mineral acid, which should be sulphuric, hydrochloric, or nitric, according to the metal present. The metals pass into the dilute acid liquid, and may be estimated by the ordinary methods of mineral analysis. The oleic acid formed from the oleate is dissolved by the ether, and may be weighed after evaporating off the solvent. Any free oleic acid, neutral fat, or hydrocarbon (*e. g.*, vaseline) which may have been present in the original substance will also be found in the ether-residue, and may be ascertained by the methods indicated on page 79 *et seq.*

With the exception of the salts of the alkali-metals, all the metallic oleates are insoluble in water, though they dissolve in many instances in alcohol, ether, carbon disulphide, and petroleum spirit. The calcium, magnesium, and iron oleates also dissolve in glycerol.

Potassium oleate is the principal constituent of soft soap. It is a white, friable, deliquescent substance, which with a small quantity of water forms a transparent jelly, soluble in alcohol or a moderate quantity of water; but decomposed on copious dilution into free alkali and a gelatinous hydrogen *oleate*, insoluble in water but readily soluble in alcohol.

Sodium oleate, m. p. 232–235°, is a constituent of hard soap. It may be prepared pure by neutralising an alcoholic solution of oleic acid with sodium hydroxide and evaporating off the alcohol. It may also be obtained by the addition of sodium carbonate to hot oleic acid. It is not deliquescent, but by contact with air becomes gelatinous. Pure sodium oleate may be obtained in crystals from its solution in absolute alcohol, but not from aqueous alcohol or from the syrupy solution in water.

Ammonium oleate is obtained in solution by treating oleic acid with cold aqueous ammonia. It is a gelatinous substance, soluble in water, and readily decomposing into ammonia and oleic acid.

Barium oleate, $Ba(C_{18}H_{33}O_2)_2$, is a light crystalline powder, insoluble in water, and difficultly soluble in boiling alcohol.

Magnesium oleate, $Mg(C_{18}H_{33}O_2)_2$, is insoluble in water, but soluble in alcohol and petroleum spirit.

Aluminium oleate is a soft, white, putty-like substance, insoluble in water, but soluble in ether and petroleum spirit. It has received a curious application, owing to its great tenacity and peculiar property of stretching into a thin string without breaking. It is made by saponifying whale, cottonseed, or lard oil with sodium hydroxide and adding the aqueous solution of the resulting soap gradually to a solution of alum. A tough, gummy precipitate of aluminium oleate, palmitate, etc., is formed, which constitutes the product known as "oil-pulp." This may be dissolved in 4 or 5 times its weight of mineral lubricating oil to form "thickener," which is employed to impart a factitious viscosity to oil.[1] Such oil will readily form threads in dropping, and has a thick, glairy character. The false viscosity thus produced cannot be regarded as really increasing the lubricating value of the

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[1] A sample of "oil-pulp," the analysis of which is given in the *Oil and Colourman's Journal*, 4, 403, had the appearance of thick gelatin or soaked glue. It had a sp. gr of 0.921, and is said to have contained:

	%
Paraffin oil of 0.906 sp. gr.	48
Lard oil (uncombined)	15
Fatty acids, 30 Alumina, 6	36
Water, soda, and loss	1
	100

oil, and the use of aluminium soap for the purpose can only be regarded as an adulteration.

Ferric oleate is dark red, but otherwise resembles the aluminium soap.

Cupric oleate is a dark green, wax-like substance, readily obtained by double decomposition. It becomes quite fluid at 100°, and dissolves with green colour in all proportions of alcohol, ether, and fixed oils.

Lead oleate, $Pb(C_{18}H_{33}O_2)_2$, is the principal constituent of the "lead plaster" of pharmacy. As obtained by double decomposition it is a light white powder, m. p. 80° to a yellow oil, and solidifying on cooling to a brittle translucent mass. Lead oleate is quite insoluble in water, but soluble in alcohol and in ether, especially when hot. It is also dissolved by oil of turpentine and by petroleum spirit, the hot saturated solution in the last solvent solidifying to a gelatinous mass on cooling. The solubility of lead oleate in ether is utilised in analysis for the separation of oleic from palmitic and stearic acids.

By boiling oleic acid with water and excess of lead oxide or basic lead acetate, a basic oleate is obtained which is nearly insoluble in ether.

Zinc oleate is a white unctuous powder, soluble in carbon disulphide and petroleum spirit.

Many of the so-called commercial "oleates" are prepared by the use of Castile soap instead of pure sodium oleate. They are better described at "oleo-palmitates," and for pharmaceutical purposes are probably equally suitable.

Oleic Esters.

Ethyl oleate is prepared by passing dry hydrogen chloride into a solution of oleic acid in three times its volume of absolute alcohol. Esterification takes place very rapidly, and the ester separates from the liquid as an oily layer. It has a sp. gr. of 0.870 at 18°, is soluble in alcohol, and is decomposed by distillation. Nitrous acid and its equivalents slowly convert it into the isomeric ethyl elaïdate.

Dodecatyl oleate and its *homologues* are said to constitute the greater part of sperm and bottlenose oils.

Glyceryl oleates are obtainable synthetically by heating oleic acid and glycerol together in sealed tubes at 200° for 24 hours. With excess of glycerol, the monolein is produced. With excess of oleic acid, *olein* is formed, and under special conditions the dioleate is said to be obtainable. Monolein and diolein are not known to occur naturally, but olein occurs in many fixed oils, and may be obtained approximately pure by agitating olive or almond oil with a cold concentrated aqueous solution of sodium hydroxide, which, it is said, saponifies the palmitin and leaves the olein mostly unchanged. After 24 hours, water is added and the soap solution separated from the oily layer, which should be washed with dilute alcohol and filtered through animal charcoal. As thus prepared, olein is a colourless, tasteless oil, readily soluble in ether or in absolute alcohol, sp. gr. 0.900 to 0.920. Pure olein is obtained when $\alpha\beta\gamma$-tribromopropane is heated with sodium oleate, it has m. p. $-5°$ to $-4°$, b. p. 235° to 240°/18 mm. (Guth, *loc. cit.*). By treatment with nitrous acid it is converted into solid elaïdin. It solidifies below 0°, can be distilled in a vacuum, and on exposure to air oxidises and becomes acid.

SOAP.

By HENRY LEFFMANN.

Soap is ordinarily understood to mean the solid amorphous material obtained by treating common fats and oils with potassium or sodium hydroxide. The process is called "saponification." This term and the term "soap" have, in chemistry, wider meanings than formerly, being applied to all processes in which esters are decomposed by metallic oxides or hydroxides, and even by some to the decomposition of esters by water with or without the coincident action of enzymes; but this class of actions is best termed "hydrolysis." For the general principles of these actions and the laboratory methods of saponification, see the section on "Esters" in Vol. 1.

All common fats and oils yield glycerol as the alcoholic product of saponification, but the salts formed differ with each fatty material, as the acid radicles are different. The waxes can also be saponified, the process being strictly analogous to that with the fats and oils; but appreciable amounts of glycerol are not obtained, and the soaps are not in common use. Although all oxides and hydroxides may have some action on esters, yet in practice the materials used are potassium hydroxide and sodium hydroxide. The former produces rather slimy masses (soft soap) the latter usually firmer bodies (hard soap). Ammonium hydroxide has a limited action. The soaps produced by potassium, sodium, or ammonium hydroxide are somewhat soluble in water and alcohol, those produced by the other hydroxides are very sparingly soluble. Potassium and sodium soaps are not extracted from solution in water by shaking with carbon tetrachloride, ether, benzene, petroleum spirit, and carbon disulphide. These solvents may be employed to separate them from unsaponified oil, fatty acids, and hydrocarbons. The characters of the pure potassium and sodium salts of the more important fatty acids have already been described.

Potassium soaps are deliquescent; sodium soaps, in the absence of free alkali, are not deliquescent. Both forms are readily soluble in hot water and alcohol; their concentrated solutions, in hot water or alcohol, form a jelly on cooling. Copious dilution of the solution with cold water or the cooling of a hot dilute solution causes the precipitation of an acid soap, while alkali or a basic soap remains in solution. This reaction has an intimate relation to the detergent properties of soap. Wright and Thompson (*J. Soc. Chem. Ind.*, 1885, 4, 630) investigated the extent to which neutral soaps of different kinds undergo hydrolysis by treatment with water, and obtained the results shown in the following table:

Nature of soap	Fatty acids		Percentage of total alkali set free by addition of x molecules of water to one molecule of anhydrous soap.				
	Nature	Mean molecular weight	$x=150$	$x=250$	$x=500$	$x=1000$	$x=2000$
Sodium stearate	Pure stearic acid.	284	0.7	1.0	1.7	2.6	3.55
Sodium palmitate ...	Nearly pure palmitic acid.	256	1.45	1.9	2.6	3.15	3.75
Sodium oleate	Pure oleic acid.	282	1.85	2.6	3.8	5.2	6.65
Coconut oil soap.....	Crude lauric acid.	195	3.75	4.5	5.4	6.45	7.1
Castor oil soap	Crude ricinolic acid.	294	1.55	2.2	3.0	3.8	4.5
Cottonseed oil soap (chiefly)	....	250	2.25	3.0	5.0	7.5	9.5
Tallow and rosin soap (primrose)	....	280	1.5	2.2	3.1	4.2	5.3
Tallow and palm oil soap	....	271	1.1	1.55	2.6	4.1	5.3

It appears from this table that the tendency of sodium laurate, palmitate, and stearate to undergo hydrolysis decreases with an increase of the molecular weight. The figures for tallow-rosin soap show that the presence of rosin soap does not materially affect the rate of hydrolysis of sodium oleate and stearate. Alkali causes a marked reduction in the extent of hydrolysis produced by a given amount of water. Thus, the tallow-rosin soap, in presence of an amount of sodium hydroxide equal to 15% used in producing the soap, underwent no decomposition by 150 molecules of water, only 0.1 by 250, and 1.3 by 2,000 parts of water. Other observers have obtained results not agreeing with the above. Rotondi found that water, especially when hot, decomposes neutral soaps into basic and acid soaps without the formation of free alkali. Basic soaps dialyse easily, are completely soluble in cold water, and are precipitated by brine without decomposition. They act as solvents for the acid soaps and free fatty acids, and emulsify fats without saponifying them. Carbonic acid renders basic soaps insoluble without the formation of free alkali; on warming the liquid re-solution takes place. Acid soaps diffuse with difficulty, are insoluble in cold water, and but little soluble in water, but are soluble in warm solutions of basic soaps. Acid soaps do not dissolve or emulsify either fatty acids or fats.

The experiments of Krapps and Stern (*Ber.*, 1894, **17**, 1747) seem to prove that hydrolysis increases with the molecular weight of the fatty acids, but this conclusion is directly opposed to that of Wright and Thompson.

Many resins, especially common rosin (colophony), form soaps with alkalies. These products are not usually commercial articles by themselves, but are found in large amount in cheap soaps.

The soaps of commerce may be divided broadly into 2 classes—*hard* and *soft*. Hard soaps are made with solid animal fats, vegetable fat oils, or free oleic acid and sodium hydroxide; for soft soaps, fish oils or vegetable drying oils are used, saponification being effected with potassium hydroxide. Hard soaps may be thus obtained if a solid fat is employed, but a potassium soap is always softer than a sodium soap produced from the same fat. The hard soaps of commerce usually consist essentially of sodium salts, the excess of alkali and glycerol having been separated, but with soft soaps no such separation is attempted, the whole being boiled down together. Hence soft soaps are more caustic than hard soaps and contain impurities. The solid white granulations, termed "figging," seen in soft soap consist of potassium stearate, and to produce them a small quantity of tallow is used in the manufacture. As the figging is commonly but erroneously regarded as a proof of good quality, it is sometimes imitated by an admixture of starch.

Soaps have been classified by W. Lant Carpenter according to their method of production:

1. Soaps produced by the direct action of fatty acids and alkali or by the decomposition of carbonates by fatty acids.

2. Soaps produced by acting on a neutral fat by the precise quantity of alkali necessary for saponification, without the separation of any waste liquid, the glycerol produced by the reaction being retained by the soap. This class includes (*a*) soaps made by the cold process, and (*b*) soaps made under pressure.

3. Soaps produced by the ordinary method of boiling in open ves-

sels, working with indefinite quantities of alkaline lye, the processes being controlled by the experience of the operator. The soaps of this class may be subdivided into (*a*) soft soaps, in which the glycerol is retained, potassium hydroxide being used; (*b*) the so-called "hydrated" soaps, with sodium hydroxide in which the glycerol is retained, and of which "marine soap" may be taken as the type; and (*c*) hard soaps, with sodium hydroxide as a base, in which the glycerol is eliminated by addition of excess of brine or lye, comprising three kinds—curd, mottled, and yellow soaps.

The so-called "cold process" of soap-making consists in mixing the fat, previously melted at as low a temperature as possible, with just sufficient sodium hydroxide solution (at about the same temperature) to effect complete saponification. The process has the advantage of being simple, and is often employed for the manufacture of the cheaper kinds of toilet soap, since the low temperature employed prevents dissipation of the perfumes added; but the saponification is apt to be incomplete, the product often containing both alkali and unsaponified oil, besides which only the purest materials are available, as the whole of the glycerol and extraneous matters are retained in the final product. Transparent toilet soaps made by the cold process are liable to contain a considerable proportion of alkali and sugar.

"Marine soap," so called from its property of forming a lather with sea-water, is made by boiling palmnut or coconut oil with sodium hydroxide solution of 1.163 sp. gr. The alkali is added gradually until the presence of a faint excess is indicated by the taste. It is often difficult to start saponification, but once begun it proceeds with rapidity, the mixture swelling up almost instantaneously to many times its volume. Additions of salt or brine, of sodium silicate, and of sugar are often made to this class of soap, samples of which may contain 70% of water.

Sodium stearate suffers no marked change in contact with 10 parts of water, while potassium stearate is converted into a thick paste or viscid solution. Sodium and potassium palmitates closely resemble the corresponding stearates. Sodium oleate is soluble in 10 parts of water and potassium oleate in 4 parts, forming a jelly with half this proportion. The consistency or hardness of soap is not dependent solely on the metal present, but is greater in proportion to the stearin and palmitin preëxistent in the oil, and less in proportion to the olein in it.

Sodium soaps are soluble in water, but insoluble in brine and other strong saline solutions. When a moderately strong solution of hard soap is precipitated by addition of common salt, the composition of the separated soap is unchanged; but from very dilute solutions acid soaps are thrown down (see page 417). Potassium soap cannot be separated in a similar manner by adding potassium chloride to its solution. If common soap is added to the solution of a potassium soap, the precipitate consists of a sodium soap, an equivalent amount of potassium chloride being formed in the solution. Concentrated solutions of alkali and carbonates also separate either potassium or sodium soap from solution, but in weak alkaline liquids soap is readily soluble. Coconut and palmnut oil soaps consist largely of sodium laurate, and require a much larger proportion of salt to separate them from their solutions than is the case with any other varieties. Hence their use on board ships, as they form a lather with sea-water. The property possessed by common salt of precipitating soap from its aqueous solution is extensively employed for separating soap from glycerol, excess of water and alkali and impurities in the materials used.

The oils and fats employed by the soapmaker are very numerous, the greater number of those classified in the tables, pages 69 to 73, doing duty in some form or under special circumstances. Besides the actual esters or neutral oils, the fatty acids obtained by saponifying palm oil, coconut oil, tallow, and other fatty oils are largely used, as are the fatty acids obtained from cottonseed oil and recovered grease. Tallow is largely employed as such, but is superseded to some extent by palm oil. Castor oil is extensively employed for making transparent toilet soaps. Lard soap is very white, solid, inodourous, and valuable for toilet use. Cottonseed oil is now employed to a large extent. Hempseed oil, saponified with potassium hydroxide, is also much used for making soft soap. The product is green, pasty, and so soft that the least addition of water renders it liquid. Ordinary "yellow soap" is usually made by saponifying tallow or palm oil with sodium hydroxide. More or less resin is always added, but the use of too large a proportion renders the soap dark, soft, too readily soluble, and too strongly caustic. Soaps made from the drying oils are usually soft and flabby, and those from fish oils usually betray their origin by their odour.

Soaps are liable to contain unsaponified oil or fatty acids on the one hand, and excess of alkali on the other. C. R. Alder Wright proposed the addition of ammonium salts, such as the sulphate or chloride, in quantity sufficient to react with the free alkali which is so objectionable an ingredient of toilet soaps. The latter may exist either as alkali or carbonate, in addition to which there may be sulphates, chlorides, silicates, traces of calcium, magnesium, aluminium, and iron compounds existing as impurities in the alkali used, common salt as a result of the precipitation of the soap with brine, and, in transparent toilet soaps, alcohol. The use of alcohol for purifying toilet soaps has the advantage of separating carbonates and neutral salts, but alkali dissolves with the soap. On subsequently evaporating the alcohol, the soap remains as a more or less translucent mass, the transparency of which can be further increased by an addition of glycerol or cane-sugar, the latter substance sometimes being present in large proportion in so-called "glycerin soaps," from most of which glycerol is absent.

Besides the foregoing accidental impurities, legitimate additions are frequently made to soap. Thus, potassium and sodium carbonates are added to "cold-water soap" to communicate the power of lathering readily with hard water and to increase the detergent properties generally; sodium silicate is often added to soap intended for manufacturing uses and, though objectionable in some cases, may be legitimate in others. Sodium aluminate is sometimes employed; and borax, which possesses some detergent properties is used. Petroleum naphtha to the extent of 10% is sometimes incorporated with soap. It is said to increase the detergent action. A soap of this kind, now largely sold, is prepared by mixing the petroleum product with a rosin soap-mass and adding this to a common soap.

Small proportions of various substances are also added to soap as colouring and perfuming agents. Mottling is produced by iron salts, ochre, ultramarine, or even more objectionable matters, such as vermilion and copper arsenite. Such additions remain as a residue on dissolving the soap in water or spirit, and should never exceed 1% even in mottled soap, and should be less in other varieties. The perfuming agents are mostly used in very small quantities and are ineffective, and in some of the medicated soaps the substances to which therapeutic properties of the soap are attributed are present in such small proportion that the same remark is applicable.

Many forms of medicated soaps are now sold. Among the substances added are carbolic and cresylic acids, thymol, naphthalene and creosote oils, petroleum, vaselin, camphor, and gelatin.

Insoluble and inert organic and inorganic substances are added to soap, either with the alleged object of imparting special characters, or manifestly to act the part of "filling" or adulterants. Among these are oatmeal, bran, sawdust, barium sulphate, steatite, china-clay, pipe-clay, fuller's earth, sand, pumice-stone, kieselguhr, chalk, and whiting. Leffmann found 33% of mineral matter in a sample of red Castile soap. The so-called "sand soaps" now largely used for scouring purposes are usually mixtures of common soap, containing much rosin and some free alkali, with finely pulverised quartz. The proportion of quartz is often over 80%. Diatomaceous earth is also used. In a sample of a much advertised soap, said to contain milk and sulphur, neither of these bodies was found, but there was much china-clay and a notable amount of free alkali.

Assay and Analysis of Soaps.—In analysing soaps care must be taken to obtain a fairly representative sample. In the case of hard soaps this is best effected by cutting a transverse slice from the middle of the bar or cake. A cylinder withdrawn from a cake by means of a cork-borer or cheese-sampler also affords a fairly good sample. The outer portion of a cake of soap may be dried out so as to be of markedly different composition from the bulk of the cake and should be rejected. In many cases it is necessary to reduce the soap to thin shavings or slices, which should be thoroughly mixed by shaking, and preserved in a well-closed bottle.

A comparative assay of different soaps can be effected in a useful and simple manner by ascertaining what measure of a standard solution of the sample must be added to a 50 c.c. of a very dilute solution of calcium chloride or sulphate solution in order to obtain a persistent lather on shaking. The soap solution is made by dissolving 10 grm. of the sample in alcohol (sp. gr. 0.920), filtering, and diluting the filtrate with the same solvent to 1,000 c.c. The test is made exactly as in estimating the hardness of waters, the soap solution being added to the standard hard water in small quantities at a time until a lather is obtained on shaking, which remains for at least 5 minutes when the bottle used for the operation is placed on its side. The standard hard water may conveniently be prepared by exactly neutralising 40 c.c. of N/10 sulphuric or hydrochloric acid by cautious addition of lime-water, and diluting the solution to 1,000 c.c. when it will have a hardness of 14 degrees of Clark's scale.

OUTLINE OF SYSTEMATIC SCHEME FOR ANALYSIS OF SOAPS.

<table>
<tr>
<td colspan="4">A.—Dry 10 grm. of the soap as described on page 423. The loss is *water*, with possible traces of alcohol and essential oils. Place the dried soap in a plaited filter, and exhaust it with redistilled petroleum spirit, in a Soxhlet tube.</td>
<td colspan="4">I.—Exhaust 10 grm. of the sample with 100 to 150 c.c. of alcohol (95%), or, preferably, absolute alcohol, avoiding exposure to air.</td>
</tr>
<tr>
<td rowspan="3">B.—**Solution** will contain any *unsaponified* and *unsaponifiable* matters, the nature of which can be ascertained, as described on page 425. Their total amount may be found by distilling the whole or an aliquot part of the solvent solution, drying the residue at 100°, and weighing.</td>
<td colspan="3">C.—**Residue.** Allow the adhering petroleum spirit to evaporate, and exhaust the residue thoroughly with boiling water. In some cases the previous drying and treatment with petroleum spirit may be omitted, in which case 10 grm. of the original soap are at once dissolved in water, and the solution shaken with petroleum spirit, if thought desirable, the solution being treated as at B.
D.—The aqueous solution is filtered, decanted, or strained from any insoluble matter.</td>
<td rowspan="3">K.—**Solution.** Add a few drops of a neutral alcoholic solution of phenolphthaleïn. If a pink colour is produced, titrate cautiously with decinormal or seminormal, acid, the volume of which required corresponds to the *free caustic alkali* of the soap. If no pink colouration be produced on adding phenolphthaleïn, titrate the liquid with decinormal caustic alkali, the volume required corresponding to *free fatty acids* (see page 437).</td>
<td colspan="3">L.—**Residue.** Dry at 100° and weigh (see page 439). Exhaust thoroughly with boiling water, and filter, decant, or strain.</td>
</tr>
<tr>
<td colspan="2">E.—**Solution.** Treat the hot liquid with a known measure of standard sulphuric acid, using a moderate excess. Agitate thoroughly, and pass the separated aqueous liquid through a filter (see page 430).</td>
<td rowspan="2">H.—**Residue.** Consists of *insoluble matters*, mineral and organic. It may be examined instead of, and in a manner similar to, Residue N.</td>
<td colspan="2">M—**Solution.** Divide into two equal parts (see page 439).</td>
<td rowspan="2">N.—**Residue** consists of *insoluble matter.* If considerable, dry at 100°, weigh, and examine as described on page 441.</td>
</tr>
<tr>
<td>F.—**Solution.** Add methyl orange and titrate with standard alkali or sodium carbonate free from chlorides. The difference between the free acid thus found and that previously added gives the equivalent of acid required to neutralise the *total alkali* of the sample. Examine the neutralised liquid as on page 431.</td>
<td>G.—**Oily Layer** consists of *fatty* and *resin acids*, and may be treated as described on page 434.</td>
<td>1.—Add methyl orange and titrate with decinormal hydrochloric acid. Volume required corresponds to *alkali* of *carbonate*, *silicate*, and *borate* present. Employ neutralised liquid for determining *sulphates*, or to test for *starch* and *gelatin*.</td>
<td>2.—Examine for *borate*, *silicate*, *aluminate*, and *sulphate* as described on page 440.</td>
</tr>
</table>

From the preceding list of the numerous substances occurring as frequent or occasional ingredients of commercial soaps, it is evident that the complete analysis of soap is sometimes a difficult and tedious operation. In the great majority of cases, however, the examination may be restricted to an estimation of the leading constituents, and of these some have a greater or less importance according to the purpose for which the soap is intended to be used.

Manufacturers' soaps should be tested for the proportions of water, total alkali, and crude fatty acids; while the percentages of hydroxide carbonate and silicate, fatty and rosin acids existing as soap, and free fatty acids and unsaponified oil are secondary determinations, though often important.

Household and laundry soaps should be tested for the proportions of water, alkali as soap, alkali in other forms, and total fatty acids. Phenol should also be determined in soap said to contain it.

Toilet and fancy soaps should be tested for water, alkali as soap, alkali in other forms, fatty and resin acids, glycerol, sugar, and insoluble matters.

Medicated soaps should be specially examined for the proportion of the active or *quasi*-active constituent said to be present, such as phenol, sulphur, thymol, tar, and vaseline.

The table on page 422 exhibits a systematic scheme for the complete analysis of even a complex soap. It is mainly based on the scheme drawn up by C. R. Alder Wright and C. Thompson, which is a modification of that of A. R. Leeds, who appears in great measure to have derived his method from the first edition of this work. With the subsequent detailed instructions and extensions it includes methods of estimating or detecting the great majority of the substances met with in commercial soaps. The plan of procedure is so arranged as to permit of the examination of ordinary soaps being very simply conducted, while allowing any special ingredient to be sought for and determined.

Water.—The proportion of water in soap is important, and its estimation requires considerable care. If the soap be a solid one, a fairly representative sample should be reduced to fine shavings by scraping with a knife. A known weight is then exposed for some time to a temperature of 40° or 50°, the heat being gradually raised to 100°, and continued at that temperature as long as loss of weight is observed. The soap should not be allowed to melt. A better method is to dissolve about 2 grm. of the soap in the minimum quantity of hot strong alcohol, and to pour the liquid on a known weight of clean dry sand, which is then exposed with frequent stirring to a temperature of 100°. The traces of *alcohol* present in transparent toilet soaps which have been purified by solution in spirit, are volatilised with the water, and if 50 or 100 grm. of the sample be mixed with sand or powdered pumice, and gradually heated in a retort to 120°, the alcohol may be deduced from the sp. gr. of the distillate. The water in soap may also be estimated rapidly, and with ample accuracy for most purposes, in a manner recommended by Watson Smith. From 5 to 10 grm. of the finely divided sample should be placed in a large porcelain crucible, set in a sand-bath which is heated by a small Bunsen flame. The soap is continually stirred with a glass rod (weighed with the crucible) having a roughed and jagged end, a peculiarity which greatly facilitates the stirring and breaking up of the lumps of soap formed toward the end of the operation. The operation is usually complete in 20 to 30 minutes, and is known to be at an end when a piece of plate-glass placed over the crucible (the flame being removed) no longer collects moisture. Care is required to prevent burning of the soap, but the odour thus developed is so characteristic that the manipulation is easily controlled. Smith finds the results trustworthy to 0.25%.

The proportion of water in soap differs greatly. In the so-called "dry soaps," and in some of the best kinds of curd soap, it does not exceed 16 to 20%, while in inferior soaps made from coconut oil it sometimes reaches 70 to 80%.

Petroleum Spirit Solution.—Under ordinary circumstances, the material dissolved from dry soap on treatment with petroleum spirit consists merely of *unsaponified fats* or of *free fatty acids*. Insignificant proportions of unsaponifiable matter natural to fixed oils may also be present, and nitrobenzene and essential oils used for scenting the soap will also be dissolved. If Yorkshire grease has been used in manufacturing the soap, the residue may contain *cholesterol*. *Cetyl alcohol* from spermaceti and *myricyl alcohol* from beeswax and carnaüba wax will also be present if these waxes have been employed. If added to the made soap, of course the unsaponified *waxes* will be dissolved out, instead of simply the solid alcohols resulting from their saponification. If the presence of waxes is suspected beforehand, or from the amount or appearance of the residue obtained on evaporating a portion of the solution, the residual soap should be further exhausted with boiling toluene, which dissolves the wax-alcohols better than petroleum spirit.

The residue from medicated soaps may also contain metallic *oleates* and free *carbolic* and *cresylic acids*, *thymol*, and *hydrocarbons*, such as vaselin and other neutral petroleum and tar products.

When the nature or amount of the residue obtained on evaporating a small aliquot part of the petroleum spirit solution indicates the desirability of further examining it, the unevaporated portion should be treated in the manner directed in the following table:

SYSTEMATIC SEPARATION OF UNSAPONIFIED MATTERS FROM SOAP.

<table>
<tr><td colspan="4">Agitate the solution in petroleum spirit with dilute hydrochloric acid, and separate.</td></tr>
<tr><td rowspan="3"><i>a.</i> Acid Solution. Examine for <i>heavy metals</i> (<i>e.g.</i>, Pb, Hg, Cu, Zn) and <i>aluminum</i>, which, if found, must have existed in the soap as <i>oleates</i>. Potassium and sodium oleates may also have been dissolved if the soap contained much hydrocarbon. If metals are found at this stage, the amount of fatty acids dissolved by petroleum spirit must be corrected to ascertain the fatty acids existing in the soap in a free state.</td><td colspan="3"><i>b.</i> Petroleum Solution. Wash free from mineral acid by repeatedly agitating with small quantities of water. Add some alcohol and titrate liquid with standard alkali and phenolphthaleïn for estimation of <i>fatty acids</i> (page 433). Separate and agitate petroleum spirit several times with small quantities of sodium hydroxide solution, separating as before.</td></tr>
<tr><td rowspan="2"><i>c.</i> Petroleum Solution. Evpaorate at a low temperature and observe odour, especially toward the end. Weigh residue and then estimate <i>unsaponified fat</i> by Köttstorfer's process (page 15). In absence of waxes, the potassium hydroxide required divided by 0.19 gives the weight of true fats, which deducted from whole residue, gives that of the <i>hydrocarbons</i>, <i>wax-alcohols</i>. If desired, these may be isolated as on page 78, and further examined.</td><td colspan="2"><i>d.</i> Alkaline Solution. Evaporate to small bulk, dilute with three measures of strong brine, and filter.</td></tr>
<tr><td><i>e.</i> Precipitate consists of sodium salts of <i>fatty acids</i> existing in the soap either in the free state or as aluminium or other metallic oleates.</td><td><i>f.</i> Solution. Acidulate with dilute sulphuric acid, and separate layer of <i>phenols</i>, or titrate portion of diluted solution with bromine, etc. (See page 426 and "Creosote Oils," Vol. III.)</td></tr>
</table>

Hydrocarbons, such as petroleum, vaselin, and coal-tar oils, are sometimes, to a considerable extent, introduced into soap. Though incapable of saponification, they may exist in notable proportion without being suspected; for if not used in excessive amount, and especially if carnaüba wax be also added, they remain in apparent solution when the soap is dissolved in water or alcohol, and, on decomposing the solution with an acid, they pass wholly into the oily layer of fatty and resin acids.

Hydrocarbons may sometimes be detected by the fluorescence exhibited by the ethereal solution of the fatty acids. If in considerable quantity, they may be partially separated by subjecting the dry soap to a gradually increasing heat, when the hydrocarbons will distil, together with any other volatile matter which may be present.

The most satisfactory means of detecting and estimating hydrocarbons in soap is to extract them by agitating the aqueous solution of the sample with ether and alkali as described below. Any *unsaponified fat* will, however, be simultaneously dissolved by the ether, and must be separated by saponifying the ether-residue with alcoholic potash, and again agitating the solution of the resultant soap with ether, or the original soap may be evaporated with alcoholic potash, and the residue dissolved in water and treated with ether.

The directions given in the foregoing table do not require further comment, except in the case of the method indicated for the determination of *phenols*. Phenol and cresylic acid, and some other substances, are dissolved on treating the soap with petroleum spirit, and can be separated from the admixed fatty acids by precipitating the alkaline solution with brine, but the method is faulty for the following reason: soaps, and especially common household and soft soaps, are liable to contain free alkali which will react with the coal-tar acids added to form bodies not dissolved by petroleum spirit, and hence the phenols obtained are only that portion not taken up by the alkali present in the soap.

The assay of soap for the percentage of *phenols* and other *coal-tar products* is most conveniently and accurately effected by the following process, which was extensively used by Allen: 5 grm. weight of the sample is dissolved in warm water with addition of from 20 to 30 c.c. of a 10% solution of sodium hydroxide, according to the proportion of phenols believed to be present. The cooled solution is then agitated with ether, and the ethereal layer separated and evaporated at a low temperature and weighed. The odour toward the end of the evaporation and that observed on heating the residue will give considerable informa tion as to the nature of the admixture. Odours suggestive of gas-tar and burning gutta-percha are very common. The alkaline liquid separated from the ether is then treated in a capacious separator with excess of strong brine, which completely removes the fatty acids as sodium salts, while the phenols remain in solution. The liquid is well agitated to cause the soap to filter and is then passed through a filter. If the soap does not coagulate, an addition of a small quantity of tallow or palm-oil soap, previously dissolved in water, will usually determine separation. The precipitated soap is washed twice by agitating it with strong brine, the washings being filtered and added to the main solution, which is then diluted to 1 litre. 100 c.c. of this solution (=0.5 grm. of the sample of soap) is then placed in a globular separator, and acidulated with dilute sulphuric acid, when it should remain perfectly clear. A precipitation at this stage indicates the incomplete removal of the fatty acids. In such case, 200 c.c. of the alkaline solution should be treated with common salt in powder, the solution filtered through a dry filter, and 100 c.c. of the filtrate acidified as before. Standard bromine-water is then added from a burette, the stopper of the separator inserted, and the contents shaken vigorously. More bromine-water is then added, and the agitation and addition repeated alternately until the liquid acquires a faint but permanent yellow tint, showing that a slight excess of bromine has been used. If crystallised phenol had been employed for making the soap, the addition of the bromine-water causes the precipitation of tribromophenol, $C_6H_3Br_3O$, in snow-white crystalline flocks, which allow the faintest yellow tint due to excess of bromine to be observed with great facility. If cresylic acid is the chief phenol present, the precipitate is milky and does not separate well from the liquid, but the end of the reaction can still be observed. The addition of a solution containing a known amount of crystallised phenol is a useful device in many cases, as the precipitate then curdles readily, and the yellow colouration can be easily seen.

The bromine solution is made by mixing in a separator one measure of saturated bromine-water with two measures of water. This solution is approximately 1%, and should be run out from the tap of the separator into the Mohr's burette used for the titration. The burette should be closely covered, and the last few c.c. of the solution contained in it should never be employed for the titration, as it is apt to have become weak. The bromine-water must be standardised immediately before or after use, by a solution of phenol of the quality that is indicated in the sample acid, according to the kind of acid the titration has indicated to have been present in the soap. This solution is made by dissolving 0.5 grm. of the phenol in 20 c.c. of a 10% solution of sodium hydroxide, together with 5 grm. of a non-phenolic soap. The solution is then precipitated with brine in the same manner as the sample, the filtrate diluted to 1,000 c.c., and 100 c.c. acidulated and titrated with the bromine used for the sample. The volume of bromine solution used is that required by 0.050 grm. of phenol of approximately the same quality as that contained in the soap.

The remaining portion of the liquid filtered from the precipitate of soap may be evaporated to a small bulk, acidified with dilute sulphuric acid, and the separated phenols measured, but the quantity is not sufficient to make the method satisfactory. It is generally better to employ the solution for the isolation of the bromo-derivatives. For this purpose it is acidified with dilute sulphuric acid (without previous concentration), and bromine-water added in slight excess. From 5 to 10 c.c. of carbon disulphide are then added, the liquid well agitated, and the carbon disulphide tapped off into a small beaker. The aqueous liquid is agitated with fresh quantities of carbon disulphide (5 of 5 c.c. each) till it no longer acquires a red or yellow colour. The carbon disulphide is then allowed to evaporate spontaneously, when a residue is obtained consisting of the brominated derivatives of the phenols present in the soap. If *crystallised* phenol of fairly good quality had been introduced into the soap, the bromo-derivative is obtained in fine long needles having very little colour, and, if all heating was avoided during the evaporation of the carbon disulphide, the weight of the residue multiplied by 0.281 gives a fair approximation to the amount of phenol; but if a crude liquid article has been employed, consisting mainly of *cresylic acid* the bromo-derivative will be deep yellow, orange, or red, with little or no tendency to crystallise, and the weight will not afford even a rough indication of the amount of coal-tar product present.

Lewkowitsch considers the following rapid process sufficiently accurate for practical purposes: A somewhat large amount of the sample, say 100 grm., is weighed off, dissolved in hot water, the solution rendered strongly alkaline with sodium hydroxide, the soap precipitated with sodium chloride, the curd separated and washed with strong sodium chloride solution, the solution boiled down of the phenolate to a small bulk, transferred to a stoppered measuring cylinder of 50 or 100 c.c. capacity, sufficient salt added so that some remains undissolved, and the liquid acidified with sulphuric acid. The volume of the separated phenols is then read off, and the number of cubic centimeters taken as so many grm.

The following table shows some of the results obtained in Allen's laboratory by the assay of representative samples of commercial carbolic soap. The descriptions given by the manufacturers are strictly adhered to. Two samples described in the same words were manufactured by different firms:

Description of soap	Phenols		Ether-residue	
	Percentage	Nature	Percentage	Odour on heating
1. Medical carbolic soap; 20% pure	30.5	Pure phenol	......	....
2. Medical carbolic soap; 20% pure	17.0	Pure phenol	4.2	Gutta-percha.
3. Carbolic toilet soap; 10%	3.6	Pure phenol	2.0	Cayenne.
4. Carbolic toilet soap; 10%	3.4	Pure phenol	1.0	Gutta-percha.
5. Transparent carbolic soap	3.2	Pure phenol	...	....
6. Transparent coal-tar soap	1.5	Pure phenol	...	....
7. Domestic carbolic soap	4.8	Pure phenol	...	....
8. Domestic carbolic soap	6.4	Common carbolic	..	....
9. No. 1 carbolic soap	5.4	Common carbolic	...	....
10. No. 2 carbolic soap	3.5	Common carbolic	...	....
11. Carbolic soap	1.1	Common carbolic	1.0	....
12. Carbolic soap	0.5	Impure carbolic	...	....
13. Carbolic soft soap; 10%	9.9	Common carbolic	...	....
14. Carbolic soft soap; 10%	8.2	Common carbolic	...	....
15. Carbolic soft soap	0.16	Common carbolic	...	....
16. Disinfectant soap	none	....	4.6	Coal-tar oils.
17. Sanitary soap	0.75	Impure carbolic	4.6	Coal-tar oils.

It will be observed that in No. 1 sample, described as containing 20% of crystallised carbolic acid, 30.5% was actually found, which result was confirmed by weighing the tribromophenol, which crystallised in well-formed colourless needles. In some cases the proportion of phenols found was notably less than the amount stated to be present, and this was especially the case with Nos. 3 and 4, though these were made by different firms. It must, however, be borne in mind that a loss of 2 or even of 3% of phenol is liable to occur through evaporation.

C. **Residue Insoluble in Petroleum Spirit.**—The portion of the sample not volatile at 100° and insoluble in petroleum spirit constitutes the *soap proper.*

In analysing soap of known origin and general composition it is often wholly unnecessary to go through the previous operations of drying and exhaustion with petroleum spirit. In such cases it is evidently preferable to weigh out 10 grm. of the original soap and at once treat it with hot water.

D. **Aqueous Solution of the Purified Soap.**—In most cases soap will dissolve almost completely in boiling water, but if a large quantity of the solvent be employed, hydrolysis occurs to a serious extent, and if such a liquid be filtered, a notable quantity of acid soap may be removed. Hence it is better, when possible, to separate any insoluble matter by decantation. When the proportion of insoluble matter is inconsiderable, there is no occasion to separate it, as with proper management it will not interfere with the subsequent operations. An exception occurs in the case of calcium carbonate, which, if not removed will neutralise acid and render the figure for the total alkali too high.

In many cases the aqueous solution of the soap may be advantageously agitated with ether at this stage. Such treatment obviates the necessity of previously extracting the dried soap with petroleum spirit, while it removes *hydrocarbons*, *unsaponified oil*, and *free fatty acids* in a very satisfactory manner. The ethereal layer having been separated (see page 22), the aqueous liquid is again shaken with ether, which is separated as before. The ethereal solution may then be treated in exactly the same manner as is directed for the petroleum spirit solution on page 425, while the aqueous liquid can be at once titrated with standard acid, though for convenience of subsequent manipulation of the fatty acids it is desirable first to remove the dissolved ether by boiling the solution in a capacious flask.

E. **Separation of Fatty Acids.**—For decomposing the aqueous solution of the soap, N/1 sulphuric acid possesses some advantages, and should be used in moderation, an excess of 5 c.c. beyond that necessary to combine with alkali present being sufficient. Wright and Thompson prefer to substitute standard nitric acid, as it enables the sulphates to be estimated by barium chloride in one portion of the filtrate, and the chlorides by silver nitrate in another.

The method of manipulation for the separation of the oily layer of fatty acids from the aqueous liquid depends on circumstances.

When the soap is chiefly a stearate or palmitate, as that made from tallow or palm oil, the liberated fatty acids are solid when cold, and in such cases there is no better plan than to effect their precipitation in a beaker or vessel of such shape that the cake can be directly removed, wiped with blotting-paper, and weighed. Precipitation in a conical flask, is advantageous in some cases.

If the fatty acids are liquid at the ordinary temperature or form a cake deficient in consistence, a known weight of dry, bleached beeswax or stearic acid may be added to the hot liquid. The fatty acids become amalgamated with the melted wax, and, on cooling, a firm coherent cake is formed, which may be at once wiped and weighed. The weight of wax added (which should be about the same as that of the soap employed) being deducted from that of the cake, the weight of the crude fatty acids is at once found.

As a rule, it is preferable to effect the decomposition of the soap solution in a stoppered separator, running off the aqueous liquid through a wet filter, and subsequently allowing the fatty acids also to run on to the filter, where they are washed with boiling water, and subsequently treated as described on page 20. This method of treatment is the best when it is desired to make a further examination of the separated fatty acids.

Coconut and palm nut oil soaps yield acids not wholly insoluble in hot water. In such cases the precipitation of the acids should be conducted in a tolerably concentrated liquid, which may be advantageously saturated with common salt. The washing of the separated acids should be restricted, and brine may be advantageously used, while the drying should be effected with as little exposure to heat as possible.

F. **Solution Separated from the Fatty Acids.**—The method described in the table for determining the *total alkali* of soap is, in most cases, highly satisfactory. The result is not affected by the omission to treat the soap with petroleum spirit before dissolving it in water, and ordinary insoluble matters do not interfere. If, however, an insoluble carbonate be present, it will neutralise acid, and must be separated, or the figure for alkali will be too high (see page 437).

Instead of at once adding an excess of standard acid, then titrating back, and thus ascertaining the volume required to neutralise the alkali of the soap, the standard sulphuric acid may be added gradually to the soap solution, until the neutral point, as indicated by methyl-orange, is reached. An excess of acid is then added and the fatty acids separated as before.

The volumetric method of estimating alkali does not distinguish between potassium hydroxide and sodium hydroxide, and hence, if the nature of the alkali present be unknown, the estimation is simply an expression of the alkali in terms of one or the other. If further information be required, the examination must be made as described on page 438.

The solution separated from the fatty acids and neutralised with standard alkali, will, of course, contain *alkali-sulphates*. In addition, it may contain many other substances, among which are, *sodium* *chloride, soluble fatty acids, glycerol, sugar, dextrin, starch, gelatin.* For the detection and estimation of these it is necessary to operate on separate aliquot portions of the solution.

If nitric acid has been used instead of sulphuric acid at the previous stage of the process, the sulphates may be estimated by precipitating an aliquot part of the solution with barium chloride.

a. Sodium chloride may be estimated by titration with decinormal silver nitrate or deduced from the weight of the silver chloride precipitate.

b. Soluble fatty acids rarely require estimation in soap. If the precautions on page 430 are adopted in separating the fatty acids from coconut and palm nut oil soaps, only insignificant quantities of soluble fatty acids will remain in the aqueous liquid. If desired, these may be determined by distilling the acidified solution, as described on page 19, but their amount may also be ascertained in the following simple manner: Titrate a certain volume of the solution with standard alkali, using phenolphthaleïn as an indicator. Titrate another portion of equal measure with the same alkali, using methyl-orange to indicate the point of neutrality. The alkali consumed in the second case corresponds to the free mineral acid only, while the difference between this and the first estimation gives the volume of alkali required to neutralise the soluble acids present. 1 c.c. of N/1 alkali corresponds to 0.144 grm. of *caprylic acid.*

Allen suggested the following as a method for estimating the total fatty acids in coconut and palm nut oil soaps as follows: Separate the fatty acids in the ordinary manner, but in as concentrated a solution as possible. Agitate the aqueous liquid with a little ether, separate, and extract any dissolved fatty acids from the ether by agitating with dilute sodium solution. Employ the alkaline solution obtained to neutralise the main quantity of fatty acids, and add a few drops of phenolphthaleïn, and then more alkali, drop by drop, until the pink colour just remains permanent. Then precipitate the hot liquid with a slight excess of magnesium sulphate, filter, wash with hot water, dry the precipitate at 100° and weigh. Ignite the precipitate and weigh the residual oxide. The difference is the weight of fatty anhydrides forming insoluble salts with magnesium. Evaporate the filtrate, dry the residue at 100°, and weigh. Ignite and weigh again. The difference is the weight of fatty anhydrides forming soluble salts with magnesium.

J. A. Wilson employs the following process in the presence of soluble fatty acids:

1. The alkali in all forms is estimated by titration with standard acid in the usual manner.

2. Another weighed quantity of the soap is decomposed in an Erlenmeyer flask with a slight excess of dilute sulphuric acid, and the flask kept on the water-bath until the fatty acids separate quite clear. The flask is placed in ice-water to cool and then filtered. The fatty acids are washed 3 times successively with 250 c.c. of boiling water, allowed to cool each time, and filtered. The united filtrates are diluted to 1,000 c.c., and 500 c.c. placed in a beaker and tinted with methyl-orange; N/10 alkali is then run in until the liquid acquires the usual colour, after which a little phenolphthaleïn is added and the addition of standard alkali continued until a permanent pink is established. The amount used in the latter titration is due to soluble acids and is calculated to caprylic acid. The fatty acids in the flask and that on the filter are dried and weighed, and then dissolved in alcohol and titrated with N/2 alkali. The amount so used, together with that required for neutralisation of the soluble acids, deducted from the total alkali, gives the alkali existing in forms other than as soap.

If desired, the soap may be decomposed with standard sulphuric acid, methyl-orange added, and the alkali required for neutralisation noted; this, deducted from the total acid used, would give the acid equivalent to the alkali existing in all forms. In this manner are ascertained:

Total alkali..
Combined alkali....................................
Insoluble fatty acids...............................
Soluble fatty acids.................................

c. Glycerol may exist in soap. In the absence of sugar, it may be estimated with considerable accuracy by the permanganate process. When glycerol is present in considerable amount in soap, Lewkowitsch makes the estimation by dissolving it in water, separating the fatty matter with acid, and filtering off. The filtrate is then neutralised with barium carbonate and boiled down to the consistency of syrup. The residue is then extracted with a mixture of 3 parts of 95% alcohol and 1 part ether, the alcoholic solution filtered and evaporated on the water-bath to small bulk, and finally dried under a desiccator. The glycerol in the residue may be estimated by the acetin method. A more convenient method is that of Hehner with potassium dichromate (see under "Glycerol"). The presence of sugar renders the above methods wholly useless, and one of the plans described below must be adopted.

d. Sugar is rarely present except in transparent toilet soaps, but in these it sometimes exists to the extent of 20 to 30% of the entire weight, or in a proportion approaching that of the anhydrous soap present. Such soap is sometimes sold as "glycerin soap," though wholly destitute of glycerol.

According to Donath and Mayrhofer (*Zeit. anal. Chem.*, 1881, 383), the estimation of sugar and glycerol may be made by adding to the solution slaked lime sufficient to combine with the sugar and an equal quantity of washed and ignited sand, boiling down to the consistency of syrup, pulverising the cooled residue and exhausting it in a closed vessel with 80 to 100 c.c. of a mixture of equal parts of ether and alcohol. The glycerol will pass into solution, and, after cautious evaporation of the solvent, may be estimated by methods given under "Glycerol."

Sugar may be estimated by Fehling's solution, after inversion, without previously separating the glycerol, but the solution should be dilute and the boiling very limited in duration, or the glycerol may cause some reduction.

In an aqueous liquid containing no other bodies than sugar and glycerol, the amount of glycerol may be deduced from the sp. gr. of the liquid. The sugar having been previously estimated by Fehling's solution or other means, its effect on the sp. gr. can be readily calculated; and this being deducted from the observed sp. gr., gives that due to the glycerol present in the liquid. See section on "Glycerol."

Organic matters, such as starch, dextrin, gelatin, may be detected by special tests; but their recognition is more easy and certain in residue L, left on treating the purified soap with alcohol.

G. **Examination of the Oily Layer of Fatty Acids.**—The separation of the liberated fatty acids from the acidified aqueous solution has already been described. If wax or stearic acid has been employed for the purpose of obtaining a solid cake, the further treatment of the fatty acids is practically limited to drying them and determining their weight. In many cases, however, it is of interest or importance to make a further examination of the oily layer, which in that case should be treated as described on page 22.

The oily layer may contain *fatty acids*, the acids of *resin* or *colophony*, *coal-tar products* which existed as salts in the original soap, and other bodies of acid character and limited solubility in water. If the treatment with petroleum spirit has been omitted, the oily layer may contain various *hydrocarbons*, *waxes* and *wax-alcohols*, *unsaponified fat*, etc. In such a case the proximate analysis is best made as indicated in the table on page 425. When only fatty and resin acids are to be estimated, they may be separated by Twitchell's method (page 77); but it must be remembered that any unsaponified oil may contaminate the resin acid and be estimated as such. Resin acids may be detected by the Liebermann-Storch test (page 310).

It is often important to ascertain the origin of the fatty acids from soap. In some cases this may be satisfactorily solved by a study of their physical and chemical properties. Thus, the melting- and solidifying-points of the fatty acids from various sources are given on pages 69 to 73, and Archbutt has communicated the following observations of the sp. gr. of the acids from several oils. The observations were made at the b. p. of water by means of a Sprengel tube, and the figures express the sp. gr. of the fatty acids at the b. p. of water, compared with water at 15.5°.

Fatty acids from	Sp. gr.	Fatty acids from	Sp. gr.
Olive oil, genuine	0.8422	Nigerseed oil	0.8546
Olive oil, genuine	0.8404	Linseed oil	0.8583
Olive oil, Gallipoli average	0.8423	Train oil	0.8580
Colza oil	0.8448	Lard oil	0.8438
Rape oil	0.8423	Tallow	0.8364
Cottonseed oil	0.8478	Palm oil	0.8367

Much information can be gained by ascertaining the combining weight as described on page 377. The figures yielded by the acids from various oils are given on page 378, and in other cases they may be calculated from the saponification equivalents recorded on page 17. The combining weight of the insoluble acids is usually less than the saponification equivalent of the oil by about 13 to 14. This statement only applies to those oils yielding about 95 to 96% of insoluble fatty acids on saponification.

Similarly, the iodine absorptions of the insoluble fatty acids (p. 378) are more or less characteristic of their origin, but are subject to the same limitations as are stated above to apply to the saponification equivalents.

In cases in which the acids are practically insoluble in water, a titration in alcoholic solution with standard alkali and phenolphthaleïn affords a simple and accurate means of ascertaining the proportion of *alkali existing in combination with the fatty and resin acids*, as it is evident that the amount of alkali required for neutralisation of the separated acids must be the same as that with which they had been previously in combination.

The fact that the soaps produced by the saponification of *coconut* and *palm nut oils* are not readily precipitated by solution of common salt, may, according to W. Lant Carpenter, be employed for detecting the presence of these oils in soap. A sufficient quantity of the soap should be dissolved in hot water, and the fatty acids liberated by acidifying the solution, and separated without special washing or use of ether. 10 grm. of the fatty acids are treated with 39 to 40 c.c. of N/1 sodium hydroxide or a volume just sufficient to dissolve them completely. The whole is then boiled and the weight of the liquid brought to 50 grm. by evaporation or cautious addition of water. A saturated solution of common salt (previously boiled with a few drops of sodium carbonate and filtered from any precipitate) is then run in gradually from a burette, the liquid being constantly stirred and kept gently boiling. The addition is continued until the soap suddenly precipitates, a point which is usually sharply marked. The soap from ordinary oils is precipitated when from 8 to 10 c.c. of the salt solution has been added, but that from coconut oil requires an addition of more than 50 c.c. Mixtures of the fatty acids from coconut or palm nut oil with those from other oils will of course require a volume of brine intermediate between these two limits.

I. **Exhaustion of the Soap with Alcohol.**—If the original soap is tolerably dry, ordinary rectified spirit is usually sufficiently strong for the treatment at this stage; but if the sample contain much water, absolute or nearly absolute alcohol should be used, or the solution will have an objectionable tendency to gelatinise during filtration and other inconveniences will arise. It is recommended by both Leeds and Wright that the portion of the soap to be treated with alcohol should be a part of that previously exhausted with petroleum spirit, but, as pointed out by C. Hope, it is not possible to dry soap effectually without a notable conversion of the alkali into carbonate. The treatment with alcohol can be effected either in the Szombathy-tube, or by boiling the soap with the solvent, and filtering and washing in the usual way.

K. **Examination of the Alcoholic Solution.**—*a.* The estimation of the *free alkali* existing in soap can be effected very simply and accurately by the method of C. Hope, described in the table, the error rarely exceeding 0.25% of the total free alkali present. The test may be applied qualitatively by dropping an alcoholic solution of phenolphthaleïn onto a freshly cut surface of the soap, when a red colouration will be produced, the intensity of which increases with the proportion of the alkali present. Caustic or carbonated alkali will also be indicated by the black or grey colouration produced by dropping mercurous nitrate on the freshly-cut surface. Each 1 c.c. of N/1 acid neutralised represents 0.0471 grm. of potassium oxide, 0.0561 of potassium hydroxide, 0.031 of sodium oxide, or 0.040 of sodium hydroxide. Should it be desired to ascertain which is present, the method described on page 439 must be employed.

It is possible to have a *negative* alkalinity shown at this stage. This result is due to the presence of fatty acid or a diacid salt, but acidity of the alcohol may produce the same effect. The volume of standard alkali required to be added before a pink colour appears should be calculated to its equivalent of *oleic acid*, which is stated in the analysis as existing in the free state. Any difference between this amount and that found in the petroleum spirit solution is due to a partial neutralisation of the free acid coexisting in the imperfectly mixed soap. The following method of treating the alcoholic solution of a soap in such a manner as to allow of the estimation of the leading constituents in a very rapid manner has been communicated to the author by C. Hope: 2 grm. of the soap are dissolved in hot absolute alcohol, a drop of phenolphthaleïn solution added, and carbon dioxide passed till any pink colouration is destroyed. The liquid is then filtered, the residue, consisting of *total impurities*, washed with hot alcohol, weighed, and then titrated with N/10 acid and methyl-orange to find the *alkali not existing as soap.* The alcoholic solution is evaporated to dryness at 100°, and the residue of *dry soap* weighed when constant. It is then ignited gently, treated with water, and the solution titrated with decinormal acid and methyl-orange to find the *alkali existing as soap.* The difference between this and the total residue before ignition gives the *fatty* anhydrides, which, multiplied by 1.03, gives the *fatty* *acids*. The *water* is found with sufficient accuracy by subtracting the sum of the weights of the impurities and dry soap from 100.00.

It is necessary to avoid confusion between the real alkali, *i. e.*, existing in a soap in the form of potassium or sodium hydroxide, the apparent alkali, which corresponds to the soap, and that corresponding to carbonate, silicate, or borate. If the estimation is made in the alcoholic solution, as recommended, the actual hydroxide will alone be present, the other compounds capable of neutralising acid being insoluble in spirit. On the other hand, the standard acid required to neutralise the aqueous solution of the soap (page 431) includes that corresponding to any soluble *carbonate*, *silicate*, and *borate* or *aluminate* in the sample.

The alcoholic solution of the soap rendered neutral to phenolphthaleïn may be conveniently employed to estimate the *alkali existing in combination with the fatty and resin acids* of the sample. To effect this, it is merely necessary to add a few drops of methyl-orange solution to the neutralised liquid, and then at once titrate with standard sulphuric or hydrochloric acid. The point of neutrality is sharply marked by the production of a pink colour, and the accuracy of the results are all that could be desired.

In order to prevent misunderstanding, the volumetric method of ascertaining the proportions of alkali existing in soap in various conditions may be recapitulated as follows:

In alcoholic solution of soap.—1. Acid required to establish neutrality to phenolphthaleïn corresponds to *free alkali*, and is calculated to oxide or hydroxide, according to circumstances. 2. Acid subsequently required by same solution to produce neutrality to methyl-orange represents the *alkali converted into soaps* of fatty and resin acids.

In residue insoluble in alcohol.—3. Acid required to produce neutrality to methyl-orange corresponds to *alkali corresponding to carbonate, silicate*, and *borate.*

In aqueous solution of soap.—4. Acid required to produce neutrality to methyl-orange corresponds to *total alkali*, whether existing as such or converted into true soap, resin soap, carbonate, silicate, borate, aluminate, and soluble lime. This estimation should therefore agree with the sum of 1, 2, and 3, or if any 2 of these have been determined the third will be the difference between their sum and the total alkali (4).

The volumetric estimation of the alkali in soap gives no information as to its nature. To ascertain this it is necessary to separate them as sulphates or chlorides. This is best effected by treating the alcoholic solution of the soap which has been used for the estimation of alkali, and is neutral to methyl-orange, with strong solution of barium hydroxide, until the formation of a permanent pink tint shows that the liquid is distinctly alkaline to phenolphthaleïn. A saturated solution of barium chloride is then added, as long as further precipitation occurs, when the liquid is filtered from the barium sulphate and barium soap. The filtrate is evaporated to dryness, and the residue cautiously ignited at the lowest possible temperature. The residue is dissolved in water, the solution filtered and treated with ammonia and ammonium carbonate, the precipitate filtered off, the filtrate again evaporated to dryness, and the residue gently ignited and weighed. In the mixed *chlorides* thus obtained, the potassium and sodium may be indirectly deduced from the percentage of chlorine present, obtained by dissolving the residue in water, and carefully titrating 1/2 of the solution with N/10 silver nitrate, using neutral potassium chromate as an indicator.

From this datum approximate calculation may be made by the following formula:

$$\text{Per cent. of sodium chloride} = \frac{\text{Per cent. of total chlorine} - 47.53}{0.1310}.$$

If greater accuracy is desired, the potassium may be estimated with platinum chloride in the usual way.

L. Residue Insoluble in Alcohol.—After drying and weighing the residue obtained at this stage, a minute quantity of it may be advantageously examined under the microscope, by which many substances will be revealed by their characteristic structure. Iodine solution will colour starch granules blue and render them more distinct.

If starch is found by the microscope, it is sometimes desirable to treat the residue with cold water, and examine the solution thus obtained separately from that subsequently obtained by the use of boiling water. Starch and gelatin will be contained in the latter only, but sodium silicate may be present in both solutions, a serious complication.

M. Examination of the Aqueous Solution of the Residue.—Before dividing the aqueous solution and titrating 1/2 with standard acid in the manner described in the table, it is sometimes desirable to make a direct estimation of the carbon dioxide evolved on treatment with acid, so as to obtain a means of calculating the amount of *soluble carbonate* present. This is necessary when the soap contains borate or silicate in addition, but otherwise the carbonate can be deduced with accuracy from the titration of the solution with standard acid. To ascertain the carbonate directly, the concentrated solution should be treated with a moderate excess of standard acid in a carbon dioxide apparatus, and the evolved carbon dioxide ascertained by the loss of weight, precipitation as barium carbonate, or measurement in a nitrometer. 44 parts of carbon dioxide correspond to 138.2 of potassium carbonate or 106 of sodium carbonate.

1. After expelling the last of the carbon dioxide by warming the acidified liquid, the solution should be divided into 2 or more equal parts, in 1 of which the excess of acid is estimated by titrating back with standard sodium carbonate and methyl-orange, and hence the sum of the alkali existing in the 4 forms of *carbonate*, *silicate*, *borate*, and *aluminate* ascertained, while the other portion is examined for borate, silicate, and aluminate as in 2.

The solution which has been employed for the estimation of the total alkali of the residue may then be divided into 2 or more equal parts, which may be employed for estimating *sulphates* by precipitation with barium chloride, *starch* by the methods described in Volume I, and to test for *gelatin* by means of tannin. If gelatin be found, it is best estimated by treating another quantity of the soap with strong alcohol and applying the Kjeldahl method to the residue. Gelatin contains about 17.9% nitrogen.

2. The other half of the aqueous solution of the residue insoluble in alcohol should be rendered distinctly acid with hydrochloric acid, and evaporated at 100° in porcelain. A slip of turmeric paper should be immersed in the liquid toward the end of the operation, and allowed to remain until the evaporation is complete. If a *borate* be present, the paper will become brownish-red in colour, and will be changed to green, blue, violet, or black on addition of sodium hydroxide solution. The residue is treated with hydrochloric acid, water added, and the solution filtered. The residue of *silica* is washed, dried, ignited, and weighed. As the *sodium silicate* present in soap is not of constant composition, though usually approximately corresponding to the formula $Na_2Si_2O_5$, it is not possible to deduce the amount of alkali existing as silicate from the weight of the silica found; but, in the absence of borates, it may be ascertained by estimating the carbon

dioxide evolved on treating the aqueous solution of the residue insoluble in alcohol with dilute acid. This estimation will give the means of calculating the alkali existing as *carbonate*, and the remainder of the alkali of the residue must exist as *silicate* (or aluminate).

The filtrate from the silica may be conveniently employed for estimating *sulphates* by precipitation with barium chloride, or of *aluminium* by precipitation with ammonium hydroxide and of *calcium* in the filtrate by precipitation with ammonium oxalate. C. Hope states that free lime is not unfrequently present in soap, and may be detected and estimated at this stage. Its presence would tend to increase the "alkali" of the residue insoluble in alcohol.

N. Residue Insoluble in Petroleum Spirit, Alcohol, and Water.—After drying the residue at 100° and noting its weight, it is desirable to examine it under a low microscopic power, with a view of recognising characteristic organic structures, which can be seen much more distinctly after the removal of the soluble matters.

Whether any further examination of the residue is requisite necessarily depends on its amount and nature and the object of the analysis. Among the various constituents of such a residue the following list comprises those most likely to be present:

1. *Insoluble Organic Matters*, such as sawdust, bran, woody fibre from oatmeal.

2. *Mineral Pigments and Colouring Matters*, as red ochre, burnt umber, various other ferruginous materials, red lead, vermilion, Scheele's green, chrome green, ultramarine.

3. *Mineral Matters used as Scourers*, such as sand, powdered quartz, pumice, and infusorial earth.

4. *Mineral Matters used as Adulterants or "Fillings,"* such as china clay, steatite, barium sulphate, chalk, and whiting.

The systematic recognition and estimation of these and other possible additions belong to inorganic analysis. It is sufficient here to indicate the following simple method of classification with a view to facilitate further examination.

Organic matters may be approximately estimated by igniting an aliquot portion of the residue. The loss will include the volatile constituents of china clay, whiting, red ochre, etc., as well as any vermilion which may be present.

By treatment with dilute hydrochloric acid, the original or ignited residue may be divided into *soluble* and *insoluble constituents*. The former include whiting, chalk, ultramarine, Scheele's green, oxide of iron, and the greater part of the ferruginous pigments; while barium sulphate, steatite, sand, quartz, pumice, kieselguhr, china clay, chrome green and vermilion are but little acted on.

Interpretation of the Results of Analysis of Soaps.—Calculating from the equation of the reaction between sodium stearate, and any strong acid, it is found sodium stearate yields 92.8% of stearic acid. Similarly, the alkali used in forming the soap would be 10.13%, so that the analysis would be—

Stearic acid	92.81%
Sodium hydroxide	10.13%
	102.94%

This statement shows an excess of nearly 3%, owing to the hydrolysis which takes place. It is evident that if the basic constituent of a soap be stated as anhydrous alkali, a correction must be made in the actual weight of fatty acid found to bring it to the corresponding quantity of anhydride. 568 parts of stearic acid correspond to 550 of stearic anhydride, and the proportions of the respective anhydrides corresponding to palmitic and oleic acids are not very different from the above. Hence in soaps made from palm oil, olive oil, and tallow the necessary correction of the observed weight of fatty acids to the corresponding quantity of fatty anhydrides may be made by multiplying by the factor 0.97, 100 parts of stearic acid representing approximately 97 of stearic anhydride. In the case of coconut and castor-oil soaps, and many others made with mixed oils, this factor is far from accurate, and hence it is in all cases decidedly preferable to determine the mean combining weight of the isolated fatty and resin acids, as described on page 377, and calculate the corresponding weight of fatty anhydride therefrom. The mean combining weight of the anhydride is always 9 less than that of the corresponding acid. The usual figures for the fatty acids isolated from various fatty oils are given on page 378.

Gassler (*J. Soc. Chem. Ind.*, 1882, 1,370) gives the following analyses of German resin soaps in comparison with Sinclair's "cold-water soap":

Description of soap	Fatty acids	Resin	Soda	Talc	Water
German soap	56.25	14.75	12.75	....	16.25
German soap	53.65	17.35	12.55	....	16.45
Sinclair's soap	46.87	23.13	12.00	1.00	18.00

Description of soap	Origin	Fatty and resin anhydrides	Sodium oxide existing as soap	Silica	Sodium oxide existing as silicate	Sodium carbonate and hydroxide	Sodium chloride	Sodium sulphate	Lime, iron oxide	Water	Total	Fatty and resin acids
1. "White," No. 1	Tallow	69.06	8.98	0.01	None.	.27	.49	.16	.07	21.14	100.18	71.20
2. "White," No. 2	Tallow and coconut oil.	60.50	6.82	0.06	None.	.06	.11	.12	.16	32.20	100.03	62.36
3. "White," No. 3	Tallow and coconut oil.	55.71	6.90	0.03	None.	.92	.18	Trace.	.08	36.54	100.36	57.44
4. "White," No. 4	Tallow and coconut oil.	44.27	6.23	7.02	2.36	.75	.32	.34	.34	38.14	99.77	45.64
5. "Cold water," No. 1...	Tallow, rosin, and cottonseed oil.	71.30	7.98	1.07	0.48	.75	.36	.30	.16	17.44	99.84	73.50
6. "Cold water," No. 2...	Tallow, rosin, and cottonseed oil.	49.95	7.00	2.34	1.01	.33	.51	.00	.50	38.18	99.82	51.50
7. "Olive oil," No. 1.....	Olive oil	71.20	7.58	0.06	0.03	.22	.66	.17	.20	19.70	99.82	73.40
8. "Marseilles," No. 1 ...	Chiefly olive oil.	62.66	7.27	0.06	0.03	.77	.76	.30	.16	28.20	100.21	64.60
9. "Palm oil," No. 1	Palm oil	59.28	6.65	0.42	0.01	.39	.47	.13	.16	32.35	99.86	61.08
10. "Mottled"	Palm nut oil....	38.89	5.76	6.40	1.29	1.62	1.78	.72	.03	38.70	95.19	40.10
11. "Satinet"	Tallow and rosin.	59.92	6.76	0.02	None.	.92	.41	.37	.05	31.30	99.75	61.77
12. Glasgow "Almond"....	Tallow and rosin.	42.41	4.14	5.64	1.59	2.76	.37	Trace.	.14	42.88	99.93	43.72
13. "Pale rosin," No. 1....	Tallow and rosin.	60.90	7.22	0.04	None.	.10	.46	.12	.02	31.22	100.08	62.78
14. "Pale rosin," No. 2....	Tallow and rosin.	48.20	5.00	0.42	1.18	.15	.65	.10	.10	45.00	99.80	49.65
15. "Pale rosin," No. 3....	Tallow and rosin.	39.92	4.70	0.62	0.25	.20	1.48	.18	.15	52.40	99.90	41.15
16. "Milling"..........	....	63.06	7.25	0.02	None.	.10	1.65	.15	.30	27.47	100.00	64.95
17. "Yellow" (for foreign markets)	....	10.90	1.36	0.03	None.	Trace.	2.57	.56	.14	84.00	99.56	11.20
18. "Marine" for emigrants	Palm nut oil....	19.42	3.11	9.00	3.98	3.00	5.13	.35	.16	53.32	97.47	20.02

Many analyses of soaps have been published, but comparatively few are trustworthy. In many cases the observers appear to have stated the amount of fatty acids and alkali as deduced from the ash, the remainder being entered as "water, etc." C. Hope furnished the valuable analytic data contained in the table on page 443. Samples 10 and 18 were prepared by the "cold process," and hence contained the glycerol produced by the saponification. This accounts for the sum of the estimated constituents being sensibly below 100.00. Samples, 3, 4, and 12 were the only three which contained free alkali, and in these it only reached the proportions of 0.16, 0.26, and 0.15% of sodium hydroxide, respectively. Hope points out that a striking feature of the analyses is the variable composition of the silicate existing in the soap, although as added it is tolerably constant in composition. This is attributed by Hope to the property possessed both by rosin and fats of taking alkali from sodium silicate, in which case the change will occur only in those soaps to which the silicate was added before saponification was complete.

W. Lant Carpenter gives the following analyses in his treatise on *Soaps and Candles*:

Description of soap	Fatty acids	Soda as soap	Soda in other forms	Silica	Neutral salts	Water	Total
Primrose soap as in south and west of England.	62.3	6.7	......	......	0.2	32.8	102.0
Primrose soap as in north of England.	42.66	5.41	1.21	0.94	0.55	50.40	101.17
Genuine "cold-water" soap	70.2	7.3	1.8	1.6	0.4	22.0	103.3
Manufacturers' neutral curd soap....	67.9	7.0	0.0	......	0.2	28.0	103.1
Manufacturers' brown oil soap, from oleic acid.	68.60	7.88	1.00	......	1.00	21.00	99.48

Partial analyses of various representative samples of carbolic soap are given on page 429.

Analyses of soft soap published show the proportion of water in samples of good quality is usually between 35 and 45%. The potassium oxide ranges from 8.8 to 11.2%.

In forming an opinion as to the quality of a soap, the application to be made of it is a primary consideration. In practice, water in moderate proportion must be regarded as a useless but unavoidable constituent; but, if present in the enormous proportion sometimes observed, it can only be regarded as an adulterant.

In some of the best brands of opaque toilet soap made by special methods, the proportion of water does not exceed 10 or 12%, but the majority of the best qualities of soap, known as Marseilles, curd, brown Windsor, honey, and primrose, contain from 17 to 24% of water. In some of the transparent toilet soaps, made by solution in alcohol, the proportion of water is very small (9 to 10%), but this advantage is more than counterbalanced by the presence of 20 to 30% of sugar. Transparent soaps made in other ways, as by the "cold process," rarely contain half their weight of actual soap, the remainder consisting of water and sugar.

Practically, the proportion of *alkali* in a soap is the best single test of its quality, but here again a distinction must be drawn between alkali existing in combination with fatty and resin acids, or, in other words, as true soap, and that existing in other conditions, particularly the caustic state. Wright arranges toilet soaps in three classes, according to the proportion the "free" or *inorganic alkali* bears to the *alkali existing as soap*. Thus, soaps containing less than 2.5 parts of free alkali for 100 of alkali as soap are arranged in the first class; those containing between 2.5 and 7.5 in the second, and those containing more than 7.5 in the third class. In judging of the quality of a toilet soap, Wright also takes into account the freedom of the soap from adulterants, "filling," water, and "closing up" agents, and from poisonous colouring matters; as also the nature and quality of the fatty matters used as basis and their freedom from rancidity.

Although the absence of a notable proportion of "free" alkali is important in the case of toilet soaps, owing to its powerful action on the skin, it does not follow that a similar absence is advantageous under other conditions. On the contrary, for scouring and household purposes, a limited proportion of alkali is advantageous, and in the case of some soaps used by manufacturers the presence of considerable proportion of alkali is essential to success, a solution of alkali with sufficient soap in it to cause lathering being preferred. A neutral soap, however pure, will for such uses be regarded as deficient in "strength," and will often cause trouble through the precipitation of free fatty acid or acid soap in the fabric with which the soap is used.

The nature and origin of the acids are sometimes of interest in judging of the suitability of a soap for certain purposes. The presence of rosin acids and of the acids from coconut or palm nut oil can be ascertained as noted under G (p. 434), and it is rarely of interest to inquire further, except in the case of soap containing coal-tar bodies, which can be examined as described on page 426.

The permissibility of additions to soap must be judged on the merits of each case, but, as a general rule, the less extraneous matters present the better. It is said that, for some purposes, as in the treatment of wool and silk, a small proportion of starch is an advantage. In contracting to supply manufacturers of textile fabrics, the soapmaker is frequently obliged to settle definitely the proportions of fatty acids, resin, alkali, and potato-starch which shall be present in the soap. A soap suitable for fulling cloth and for other purposes should not contain less than 40% of fatty acids nor more than 5% of rosin and 6 of potato-starch.

Dextrin, sugar, starch, Irish moss, and gelatin are in most cases purely adulterants, as also are kaolin, barytes, and other insoluble earthy matters; but soluble carbonates, silicates, and borates have marked detergent properties.

In a complete analysis of a soda soap, the constituents may be stated in the following manner:

	%	%
[1]Fatty anhydrides	—	—
[2]Soda existing as soap	—	
Silica	—	—
[2]Soda existing as silicate	—	
[2]Sodium carbonate	—	
[2]Sodium hydroxide	—	
Sodium sulphate	—	
Sodium chloride	—	
Calcium oxide	—	
Ferric oxide	—	
Water	—	
	—	

1 = Fatty acids—%.
2 = Total detergent alkali, as sodium oxide—%.

GLYCEROL.

(GLYCERIN.)

BY W. A. DAVIS, B. Sc., A. C. G. I.

Glycerol is obtained by the saponification or hydrolysis of fats and oils, which are mixtures of glyceryl esters of palmitic, stearic, and oleic acids principally (see p. 7). As it is always formed in small quantities during the fermentation of sugar, it is a constant constituent of fermented liquors. The name glycerol will be used in this article to refer to the chemical individual $\alpha\beta\gamma$- trihydroxypropane, the term glycerin being restricted to commercial varieties of glycerol.

Pure glycerol is a colourless, odourless, very viscous liquid, with a sweet taste. M. p. 17° (Henninger, *Ber.*, 1875, **8**, 643); 20° (Nitsche, *Jahresber.*, 1873, 323). B. p. 290°/760 mm. (corr.) (Mendeléeff, *Annalen*, [16], 1860, **114**, 117); 210°/50 mm. (Bolas, *Trans.*, 1871, **9**, 84); 179.5/12.5 mm. (Scheij, *Rec. Trav. Chim.*, 1899, **18**, 181); 162–163°/10 mm. (Richardson, *Trans.*, 1886, **49**, 764); 143°/0.2 mm. (Fischer and Harries, *Ber.*, 1902, **35**, 2158). The following table gives the sp. gr. and refractive index of carefully purified, anhydrous glycerol at different temperatures according to Scheij (*Rec. Trav. Chim.*, 1899, **18**, 181):

	Sp. gr.	N_D
20°	1.2604	1.47289
40°	1.2471	1.46866
60°	1.2339	1.46320
80°	1.2207	1.45830

The glycerin used, distilled between 162 and 163° under 10 mm. pressure; the sp. gr. values are with reference to water at 4°.

The following tables give the values obtained by different workers for the sp. gr. and refractive index of purified glycerol and of its aqueous solutions. The values given by Lenz (*Zeit. anal. Chem.*, 1880, **19**, 297) are generally regarded as the most accurate; he employed glycerol the composition of which was calculated from an elementary analysis. Strohmer (*Monatsh.*, 1884, **5**, 61) used crystals of glycerol from which adhering liquid had been removed by pressure. Gerlach's glycerol (*Die chem. Ind.*, 1884, **7**, 281) boiled constantly at 290°. Nicols' values are given in *Pharm. J.*, 1887 [3], **18**, 302; the glycerol boiled constantly at 210° under 50 mm. and was a practically pure substance as judged by a combustion. The values recently given by Martinez-Strong (*Anal. Fis. Quim.*, 1908, **6**, 75) are of doubtful accuracy.

SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS OF PURE GLYCEROL.
(LEWKOWITSCH.)

	Lenz	Strohmer	Gerlach		Nicol
Glycerin %	Sp. gr. at 12–14°/12°	Sp. gr. at 17.5°/17.5°	Sp. gr. at 15°/15°	Sp. gr. at 20°/20°	Sp. gr. at 20°/20°
100	1.2691	1.262	1.2653	1.2620	1.26348
99	1.2664	1.259	1.2628	1.2594	1.26091
98	1.2637	1.257	1.2602	1.2568	1.25832
97	1.2610	1.254	1.2577	1.2542	1.25572
96	1.2584	1.252	1.2552	1.2516	1.25312
95	1.2557	1.249	1.2526	1.2490	1.25052
94	1.2531	1.246	1.2501	1.2464	1.24790
93	1.2504	1.244	1.2476	1.2438	1.24526
92	1.2478	1.241	1.2451	1.2412	1.24259
91	1.2451	1.239	1.2425	1.2386	1.23990
90	1.2425	1.236	1.2400	1.2360	1.23720
89	1.2398	1.233	1.2373	1.2333	1.23449
88	1.2372	1.231	1.2346	1.2306	1.23178
87	1.2345	1.228	1.2319	1.2279	1.22907
86	1.2318	1.226	1.2292	1.2252	1.22636
85	1.2292	1.223	1.2265	1.2225	1.22365
84	1.2265	1.220	1.2238	1.2198	1.22094
83	1.2238	1.218	1.2211	1.2171	1.21823
82	1.2212	1.215	1.2184	1.2144	1.21552
81	1.2185	1.213	1.2157	1.2117	1.21281
80	1.2159	1.210	1.2130	1.2090	1.21010
79	1.2122	1.207	1.2102	1.2063	1.20739
78	1.2106	1.204	1.2074	1.2036	1.20468
77	1.2079	1.202	1.2046	1.2009	1.20197
76	1.2042	1.199	1.2018	1.1982	1.19925
75	1.2016	1.196	1.1990	1.1955	1.19653
74	1.1999	1.193	1.1962	1.1928	1.19381
73	1.1973	1.190	1.1934	1.1901	1.19109
72	1.1945	1.188	1.1906	1.1874	1.18837

SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS OF PURE GLYCEROL. (LEWKOWITSCH.)—*Continued.*

	Lenz	Strohmer	Gerlach		Nicol
Glycerin %	Sp. gr. at 12–14°/12°	Sp. gr. at 17.5°/17.5°	Sp. gr. at 15°/15°	Sp. gr. at 20°/20°	Sp. gr. at 20°/20°
71	1.1918	1.185	1.1878	1.1847	1.18565
70	1.1889	1.182	1.1850	1.1820	1.18293
69	1.1858	1.179	—	—	1.18020
68	1.1826	1.176	—	—	1.17747
67	1.1795	1.173	—	—	1.17474
66	1.1764	1.170	—	—	1.17201
65	1.1733	1.167	1.1711	1.1685	1.16928
64	1.1702	1.163	—	—	1.16654
63	1.1671	1.160	—	—	1.16380
62	1.1640	1.157	—	—	1.16107
61	1.1610	1.154	—	—	1.15834
60	1.1582	1.151	1.1570	1.1550	1.15561
59	1.1556	1.149	—	—	1.15288
58	1.1530	1.146	—	—	1.15015
57	1.1505	1.144	—	—	1.14742
56	1.1480	1.142	—	—	1.14469
55	1.1455	1.140	1.1430	1.1415	1.14196
54	1.1430	1.137	—	—	1.13923
53	1.1403	1.135	—	—	1.13650
52	1.1375	1.133	—	—	1.13377
51	1.1348	1.130	—	—	1.13104
50	1.1320	1.128	1.1290	1.1280	1.12831
45	1.1183	—	1.1155	1.1145	1.11469
40	1.1045	—	1.1020	1.1010	1.10118
35	1.0907	—	1.0885	1.0875	1.08786
30	1.0771	—	1.0750	1.0740	1.07469
25	1.0635	—	1.0620	1.0610	1.06166
20	1.0498	—	1.0490	1.0480	1.04884
15	1.0374	—	—	—	1.03622
10	1.0245	—	1.0245	1.0235	1.02391
5	1.0123	—	—	—	1.01184
0	1.0000	—	1.0000	1.0000	1.00000

TABLES OF THE REFACTIVE INDEX, N_D AT 12.5 TO 12.8° OF AQUEOUS SOLUTIONS OF GLYCEROL (LENZ).

% anhydrous glycerol	N_D	% anhydrous glycerol	N_D	% onhydrous glycerol	N_D
100	1.4758	66	1.4249	32	1.3745
99	1.4744	65	1.4231	31	1.3732
98	1.4729	64	1.4213	30	1.3719
97	1.4715	63	1.4195	29	1.3706
96	1.4700	62	1.4176	28	1.3692
95	1.4686	61	1.4158	27	1.3679
94	1.4671	60	1.4140	26	1.3666
93	1.4657	59	1.4126	25	1.3652
92	1.4642	58	1.4114	24	1.3639
91	1.4628	57	1.4102	23	1.3626
90	1.4613	56	1.4091	22	1.3612
89	1.4598	55	1.4079	21	1.3599
88	1.4584	54	1.4065	20	1.3585
87	1.4569	53	1.4051	19	1.3572
86	1.4555	52	1.4036	18	1.3559
85	1.4540	51	1.4022	17	1.3546
84	1.4525	50	1.4007	16	1.3533
83	1.4511	49	1.3993	15	1.3520
82	1.4496	48	1.3979	14	1.3507
81	1.4482	47	1.3964	13	1.3494
80	1.4467	46	1.3950	12	1.3480
79	1.4453	45	1.3935	11	1.3467
78	1.4438	44	1.3921	10	1.3454
77	1.4424	43	1.3906	9	1.3442
76	1.4409	42	1.3890	8	1.3430
75	1.4395	41	1.3875	7	1.3417
74	1.4380	40	1.3860	6	1.3405
73	1.4366	39	1.3844	5	1.3392
72	1.4352	38	1.3829	4	1.3380
71	1.4337	37	1.3813	3	1.3367
70	1.4321	36	1.3798	2	1.3355
69	1.4304	35	1.3785	1	1.3348
68	1.4286	34	1.3772	0	1.3330
67	1.4267	33	1.3758		

Although solid glycerol melts at a temperature slightly above the normal temperature of the air, liquid glycerol solidifies only when cooled to −40°; it then forms a gum-like mass. When glycerol is maintained, however, during a long period at a temperature of 0°, crystals of glycerol gradually separate; the crystals are hard and gritty, but deliquescent. Their formation is facilitated by the addition of a ready-formed crystal to the cooled liquid.

Glycerol is not appreciably volatile at the ordinary temperature and pressure but evaporates to a measurable extent at 100°. Contrary to the statements of Nessler and Barth, Hehner has shown (*Analyst*, 1887, **12**, 65) that glycerol is not volatilised with aqueous vapour from dilute solution. When a solution is evaporated at the b. p., appreciable loss does not occur until the solution contains about 70% (see page 457). It is highly hygroscopic, absorbing as much as half its weight of water when exposed to damp air. It is miscible with water in all proportions.

Glycerol is neutral in reaction and acts as an antiseptic, even when largely diluted; but by schizomycetic fermentation it yields *n*-butyl-alcohol and 1 : 3-propane-diol. It is miscible in all proportions with alcohol, but is insoluble in chloroform, benzene, petroleum spirit, carbon disulphide, or fixed oils, and nearly insoluble in ether, from which it separates any alcohol or water. It is soluble in a mixture of 2 volumes of absolute alcohol and 1 volume of ether—a fact which may be employed to separate it from the sugars, gums, gelatin, and various salts. Another useful solvent is a mixture of equal weights of chloroform and alcohol, in which liquid the sugars, dextrin, gums, and many extractives are insoluble.

Glycerol possesses remarkable solvent properties, dissolving many substances with greater facility than does water. This is true of iodine, phenol, mercuric iodide, and the alkaloids. Even silver chloride is very sensibly soluble in glycerol. Glycerol also dissolves potassium and sodium hydroxides, potassium sulphate and chloride, the corresponding sodium and copper salts, the vegetable acids, and all deliquescent salts. It removes ferric chloride, ferric thiocyanate, auric chloride, and some other substances from ethereal solution on agitation with them.

The precipitation of chromic solutions by ammonia and of cupric solutions by fixed alkalies is wholly or partially prevented by the presence of glycerol. With the alkaline earths and lead oxide glycerol forms compounds which are soluble in water, and give solutions which are not decomposed by carbonic acid.

When gently heated with solid potassium hydroxide, glycerol is converted into potassium acetate and formate, with evolution of hydrogen. When heated with a dehydrating agent (*e. g.*, concentrated sulphuric acid) irritating fumes of acroleïn (acrylic aldehyde), $CH_2 : CH.CHO$, are evolved, smelling like burning fat. Glycerol is very readily oxidised to carbon dioxide and water, but when carefully treated with nitric acid it is converted into a mixture of oxidation products in which oxalic acid, glyceric acid ($C_3H_6O_4$), and other organic acids occur. The substance "glycerose," obtained by the regulated oxidation of glycerol by bromine and alkali, is exclusively *sym.*-dihydroxyacetone, $OH.CH_2.CO.CH_2.OH$ (Wohl and Neuberg, *Ber.*, 1900, **33**, 3098 and 3109). By treatment in dilute aqueous solution with potassium permanganate, in presence of excess of alkali hydroxide, glycerol is oxidised in a very definite manner with formation of oxalic and carbonic acids. By treatment with potassium dichromate and sulphuric acid, it is completely oxidised to carbon dioxide and water. These changes are utilised in the estimation of glycerol (see page 458).

When a mixture of glycerol with an aqueous solution of pure mercuric chloride (free from reducing substances) is exposed to direct sunlight, calomel is precipitated after an interval of about 2 hours; the liquid shows an acid indication and gives the test for an aldehyde. It is thought that the following action occurs:

$$C_3H_8O_3+2HgCl_2=Hg_2Cl_2+2HCl+OH.CH_2.CH(OH).CHO.$$

Ferric chloride behaves similarly. After the action, the transformed glycerol has the property of dissolving the ferric hydroxide formed on adding an excess of potassium hydroxide: a carbohydrate thus appears to be formed (Archetti, *Chem. Zeit.*, 1902, 26, 555).

Glycerol Esters.—By treatment with a cold mixture of fuming nitric and concentrated sulphuric acid, glycerol is converted into glyceryl nitrate or "nitroglycerin," $C_3H_5(O.NO_2)_3$.

On mixing glycerol with strong sulphuric acid, a compound of the formula $OH.CH_2.CH(OH).CH_2.OSO_3H$ is produced, which has acid properties and forms soluble but unstable barium, calcium, and lead salts.

The so-called "glycerylphosphoric acid" (glycerophosphoric acid), obtained by heating glycerol with phosphoric acid (compare Power and Tutin, *Trans.*, 1905, **87**, 249), appears to be a mixture of α-glycerylphosphoric acid, $OH.CH_2.CH(OH).CH_2.O.PO_3H_2$, and β-glycerylphosphoric acid, $(OH.CH_2)_2.CH.O.PO_3H_2$ (Tutin and Hann, *Trans.*, 1906, **89**, 1749). A somewhat differently constituted mixture of the same acids is obtained by the hydrolysis of lecithin, a complex compound of these acids with choline and the fatty acids, stearic acid and palmitic acid, occurring in the yolk of egg and in brain tissue. For the estimation of glycerophosphates, see A. Astruc, *J. Pharm.*, 1898, [6], **7**, 5; A. Trillat, *ibid.*, 163; Imbert and Pagès, *ibid.*, 378).

Glycerol dissolves large quantities of arsenious oxide to form a compound of the formula $C_3H_5AsO_3$, glyceryl arsenite, which has been employed by calico-printers for fixing aniline colours. It is an amber-yellow, fatty substance, melting at 50° to a thick liquid which is soluble in glycerol and in water, but is decomposed by excess of the latter liquid.

When 3 parts of glycerol are heated to about 160° with 2 of boric acid, glyceryl borate, $C_3H_5BO_3$, is formed, which has been patented as a preservative agent under the name of "boroglyceride."

By heating glycerol with organic acids, esters are formed, having a composition dependent on the conditions of their formation. These esters are generally called glycerides and are specifically designated by names ending in *in*, the mono-, di-, and tri-acetates being called, respectively, monacetin, diacetin, and triacetin. Similarly, stearic acid gives rise to stearins, oleic acid to oleins, butyric acid to butyrins, and so forth. The stearins, palmitins, and oleins have already been described.

Detection of Glycerol.—When in a state of reasonable purity and concentration, glycerol may be recognised by its physical properties, no other substance likely to be met with exhibiting the combined characters of a dense viscous liquid of sweet taste and neutral reaction; miscible with water and alcohol in all proportions; volatile at a high temperature; burning with a blue flame when kindled, and leaving no carbonaceous residue.

The most characteristic property of glycerol is its behaviour when heated in a concentrated state with potassium hydrogen sulphate, whereby it is converted into acroleïn, C_3H_4O, with elimination of the elements of water. The acroleïn is recognisable by its extremely penetrating odour, resembling that of burning fat, and its property of causing a flow of tears. If the vapours be passed into water, the warm solution will be found to have the properties of an aldehyde, *e. g.*, of reducing ammoniacal silver nitrate, with formation of a mirror of metallic silver.

This test is recommended by Grünhut (*Zeit. anal. Chem.*, 1899, **38**, 37) as the best qualitative test for glycerol. The substance supposed to contain glycerol is mixed with twice its weight of potassium hydrogen sulphate and strongly heated until it foams; the vapours are led into a test-tube cooled with a freezing mixture. The distillate smells distinctly of acroleïn if glycerol is present. To confirm, add a few drops of a mixture of solutions of 3 grm. of silver nitrate in 30 grm. of ammonia of 0.923 sp. gr. and 3 grm. of sodium hydroxide in 30 grm. of water. The silver mirror should form in the cold.

The following tests are less characteristic:

If 2 drops of concentrated glycerol are treated in a dry test-tube with 2 drops of fused phenol and the same quantity of strong sulphuric acid and the mixture is heated very cautiously over a flame to about 120°, a brownish-yellow mass will be produced, which, after cooling, dissolves in water, to which a few drops of ammonium hydroxide have been added, with a splendid carmine-red colouration.

According to Reichl, minute quantities of glycerol can also be detected by boiling the solution to be examined with a minute quantity of pyrogallol and a few drops of sulphuric acid diluted with an equal volume of water, when a red colour will be produced, changing to violet-red on adding stannic chloride. Carbohydrates and various alcohols give similar results.

In common with other polyhydric alcohols, glycerol acts on borax to form a compound having an acid indication to litmus, whereas the original aqueous solution of borax is alkaline. In the case of glycerol, glyceryl borate, $C_3H_5BO_3$, is formed, together with sodium metaborate $NaBO_2$. The test may be made both in the wet and the dry way. Senier and Lowe (*Trans.*, 1878, **33**, 438) recommend that the solution to be examined should be made faintly alkaline to litmus with a dilute solution of soda, and a bead of borax (made by fusing the salt on a loop of platinum wire) dipped into it. The bead is allowed to rest for a few minutes, so as to allow solution to take place on its surface, and is then held in the flame of a Bunsen burner. A more delicate plan is to place some powdered borax in a watch-glass, pour on it some of the faintly alkaline liquid to be tested, and, by means of a looped platinum wire, introduce some of the mixture into the flame. In either case a deep-green flame will be produced if a moderate quantity of glycerol be present, but the test becomes indistinct if the liquid contains less than 5%. For detecting glycerol in beer, wine, milk, etc., 50 or 100 c.c. of the liquid should be evaporated to dryness on the water-bath, the residue extracted with absolute alcohol, the solution so obtained again evaporated, and the resultant residue moistened with a few drops of water and tested with borax as above described. Ammonium salts, glycol, and erythritol give a similar indication to glycerol. Ammonium salts may be thoroughly removed by evaporating the original liquid with sodium carbonate.

The interaction of glycerol with borax has been very thoroughly studied by W. R. Dunstan (*Pharm. J.*, 1884, [3], **4**, 41), who recommends the following mode of procedure: To 2 c.c. of a dilute solution of borax in water (1 part in 200) sufficient of an alcoholic solution of phenolphthaleïn is added to colour the liquid rose-red. The liquid to be tested for glycerol is rendered neutral or very faintly alkaline to litmus, and gradually added to the borax solution until the rose colour is discharged. The liquid is then heated to boiling, when the red colour will be restored, to disappear again on cooling the solution. Excess of glycerol is to be avoided, otherwise the alkalinity of the solution, to which the pink colouration is due, is only partially restored by boiling. Using 2 c.c. of the borax solution, about 5 c.c. of a 2% solution of glycerol must be added to destroy the colour, and the limit of sensitiveness is practically reached with a solution of this strength. The indication is also given by mannitol, erythritol, dextrose, lævulose, lactose, and mycose, but not by sucrose. Guaiacol, pyrogallol, and saligenol also respond to the test. Orcinol and resorcinol, when added in large quantity, partially destroy the red colour, but it is not restored by boiling. The test is a more delicate one for mannitol than for glycerol, and the influence of dilution is not so great. Ammonium salts discharge the red colour, but it is not restored on heating.

Estimation of Glycerol.—The accurate estimation of glycerol, when existing in a complex mixture together with other neutral organic and inorganic matters, cannot be said to have received a satisfactory solution under all circumstances. The problem is complicated by the fact that solutions of glycerol cannot be highly concentrated without serious loss from volatilisation, and that the presence of glycerol materially increases the solubility of many substances in aqueous and alcoholic solutions.

In general, the first process in the estimation of glycerol consists in separating it from the other substances with which it is mixed or combined so as to obtain it in a state of approximate purity. This can frequently be effected qualitatively in a very satisfactory manner, but it too often happens that the evaporations which are necessary steps in the process cause such a loss of glycerol by volatilisation as to render the result of little value for quantitative purposes. Proteins and some other foreign substances may be separated from a solution containing glycerol by adding a solution of basic lead acetate, and subsequently removing the excess of lead from the filtered solution by means of hydrogen sulphide. This method may be employed for the analysis of pharmaceutical preparations, such as "glycerol of tannic acid" and "glycerol of gallic acid," and is useful as one stage of the treatment of soap lyes for the estimation of glycerol.

Proteins and some other organic substances can often be removed completely by precipitating the slightly alkaline solution with zinc choride. The precipitate is filtered off and the filtrate rendered faintly acid, when a further precipitation will often occur. The last traces of zinc may be removed from the solution by potassium ferrocyanide, which is also a very perfect precipitant of albumin.

Dilute glycerol may be further purified by evaporating off the water at as low a temperature as possible, and treating the residue with absolute alcohol, a mixture of alcohol and ether or a mixture of alcohol and chloroform, according to circumstances. Absolute alcohol readily dissolves glycerol, while many classes of salts (*e. g.*, metallic sulphates, phosphates, tartrates, etc.) are insoluble. The alkali-metal chlorides are not completely separated by alcohol alone, but a mixture of equal volumes of absolute alcohol and dry ether leaves them undissolved. The same solvent serves to separate glycerol from sugar, but the use of a mixture of two volumes of absolute alcohol with one of chloroform is preferable. If the filtered solution be treated with about twice its volume of water, chloroform separates from the diluted alcohol, and often carries troublesome colouring matters with it.

Any process of estimating glycerol which involves the evaporation of an aqueous or alcoholic solution and isolation of the glycerol in substance is deficient in quantitative accuracy, as evaporation of glycerol in the latter end of the concentration is unavoidable, and the loss from this cause is often very considerable. Even absolute glycerol is sensibly volatile at 100°, the loss of weight varying with the mode of heating, the shape and material of the containing vessels, and the surface exposed.

The following figures, due to Nessler and Barth (*Zeit. anal. Chem.*, 1884, **23**, 323), show the rate of evaporation of glycerol under different conditions. The experiments were made with glycerol which had been heated for 6 hours over a water-bath at 100°, and then for 6 hours longer in an air-bath heated at 100°. In one series of experiments the glycerol was exposed in a water-oven at 100° in a platinum dish 20 mm.

high and 80 mm. diameter at the top, and 60 at the bottom; in the other, it was heated in a beaker of thin glass 40 mm. high and 48 mm. in diameter:

	Platinum dish	Glass beaker
1.0 grm. lost, in first 2 hours........	46 mg.	36 mg.
1.0 grm. lost, in second 2 hours......	29 mg.	14 mg.
1.0 grm. lost, in third 3 hours.......	21 mg.	5 mg.
Average for last 3 hours.........	7 mg.	1.7 mg.
0.5 grm. lost in first 2 hours.........	36 mg.	45 mg.
0.5 grm. lost in second 2 hours......	28 mg.	11 mg.
0.5 grm. lost in third 3 hours........	23 mg.	6 mg.
Average for last 3 hours........	7.7 mg.	2 mg.

The following figures show the loss of weight when heated on an open water-bath kept briskly boiling:

	Platinum dish	Glass beaker
1.0 grm. lost, in 1 hour,....	37–39–29–30 mg.	30–18 mg.
0.5 grm. lost, in 1 hour.....	34–29–24–30 mg.	11– 2 mg.

Other experiments conducted in platinum and glass vessels of various diameters showed that the loss increased with the diameter of the vessel (*i. e.*, with the surface of glycerol exposed), and that the rate of evaporation was less in a vessel composed of a material of low conducting power.

The volatilisation of glycerol during the evaporation of an aqueous liquid may be prevented by adding an excess of lime, which forms a compound with it, but Clausnizer has shown (*Zeit. anal. Chem.*, 1881, **20**, 58) that from the product the glycerol cannot be dissolved by absolute alcohol; and if hydrated alcohol is employed, alkalies resulting from the action of the lime on phosphates may pass into the alcoholic liquid, and carry with them substances not otherwise soluble. Even if excess of lime be avoided, the glycerol cannot be extracted completely from the residue by *cold* alcohol or ether-alcohol.

General Methods for the Estimation of Glycerol.

It will be convenient first to consider the general methods used in estimating glycerol, and then to deal later with the application of these methods to special cases; as, for example, to soap lyes or commercial forms of glycerin.

Chemical Methods. A. Volumetric.

1. *Permanganate Oxidation Process.*—This is best carried out by Benedikt and Zsigmondy's modification (*Chem. Zeit.*, 1885, **9**, 975)

of Wanklyn and Fox's method. 0.2 to 0.3 grm. of the concentrated glycerin (or a quantity of dilute glycerin corresponding to this amount and calculated approximately from the sp. gr. of the sample) is mixed with 250 c.c. of water in a large flask, 10 grm. of solid potassium hydroxide added, and a 5% solution of potassium permanganate run in at the ordinary temperature until the liquid ceases to be green and becomes blue or black in colour. Finely powdered potassium permanganate can be used in place of its solution. The mixture is then boiled, when hydrated manganese dioxide is precipitated and the solution becomes red. A solution of sulphurous acid or of sodium sulphite is then cautiously added, *drop by drop*, until the liquid just becomes colourless, and the solution then filtered through a filter sufficiently large to take at least half the liquid at one time. The precipitate is thoroughly washed with hot water. The last washings sometimes become turbid owing to the formation of manganese hydroxide, but the turbidity disappears on adding acetic acid so as to render the solution acid before precipitating with calcium chloride. The precipitation is effected by adding 10 c.c. of a 10% solution of calcium chloride to the boiling liquid. The calcium oxalate is left for some time in order to complete the precipitation, collected on a filter, and, after washing thoroughly with hot water, is transferred to a flask and titrated with N/10 permanganate in the usual way.

1 c.c. N/10 permanganate (corresponding with 0.0045 grm. $H_2C_2O_4$) = 0.0046 grm. glycerol.

In the permanganate method, excess of sulphurous acid must be carefully avoided, as in presence of hydrated manganese dioxide it destroys oxalic acid. Allen suggested the use of sodium sulphite instead of sulphurous acid, but on adding acetic acid before precipitation, sulphurous acid is liberated, which in presence of the small quantity of manganese dioxide which has passed through the filter causes the loss of oxalic acid. There is, moreover, the danger of calcium sulphite being precipitated with the calcium oxalate.

Herbig has therefore suggested the use of hydrogen peroxide in place of sulphite, and employs a smaller quantity of potassium permanganate. Mangold (*J. Soc. Chem. Ind.*, 1891, **10**, 803) reports favourably on the method, and recommends the following procedure: To 0.2–0.4 grm. of glycerol, dissolved in 300 c.c. of water containing 10 grm. potassium hydroxide, as much of a solution containing 5% potassium permanganate is added as will correspond with 1.5 times the theoretical quantity of glycerol (for 1 part glycerol 6.87 parts of potassium permanganate). The operation is conducted in the cold and the solution must be agitated on adding the permanganate. After standing for about half an hour at ordinary temperature, sufficient hydrogen peroxide is added to completely decolourise the liquid. The whole is now made up to 1,000 c.c. well shaken, and 500 c.c. filtered through a dry filter. After heating the filtrate for half an hour to destroy all hydrogen peroxide, and cooling to about 60°, sulphuric acid is added and the liquid titrated with permanganate. Heating after addition of the permanganate is superfluous. A number of results of analysis by the above method are given, which prove it to be accurate even in the presence of 90% of butyric acid.

2. *Oxidation with potassium dichromate* (*Hehner's method*). The solutions required are as follows:

1. Potassium dichromate solution, containing in 1,000 c.c. about 74.86 grm. of potassium dichromate and 150 c.c. of strong sulphuric acid. The exact oxidising value of the solution must be ascertained by titration with solutions of known quantities of iron wire or pure ferrous ammonium sulphate.

2. Ferrous ammonium sulphate solution containing about 240 grm. in 1,000 c.c.

3. Potassium dichromate solution 1/10 the strength of No. 1. The ferrous solution is exactly standardised upon the stronger dichromate solution, 1 c.c. of which should correspond to 0.01 grm. glycerol.

With pure glycerol, the oxidation is quantitative. Crude glycerols must be treated as follows: For the removal of chlorine and of aldehydic compounds, some silver oxide is added to a weighed quantity of the sample (about 1.5 grm.), which is placed in a 100 c.c. flask. After slight dilution the sample is allowed to stand with the silver oxide for about ten minutes. Basic lead acetate is then added in slight excess, the bulk of the fluid made up to 100 c.c., and a portion filtered through a dry filter; 25 c.c. of the filtrate are placed in a beaker previously well cleaned with sulphuric acid and potassium dichromate to remove all traces of fat, from 40 to 50 c.c. of the standard dichromate are added, accurately measured, and about 15 c.c. of strong sulphuric acid, and the beaker, covered with a watch-glass, is heated for 2 hours in boiling water. After that time the excess of dichromate is titrated back with ferrous ammonium sulphate solution.

As the dichromate solution is necessarily a somewhat strong one, the measurements must be made with the greatest care, attention being paid to the temperature. The results upon repetition agree well. The method is easy and rapid. It is open to the objection that by precipitation by lead acetate the impurities may not be perfectly removed, anything left being oxidised and counted as glycerol. However, all higher fatty acids and all resin acids, as well as albuminoids, sulphides, thiocyanates, and aldehydes, are completely removed, and the lower fatty acids, such as acetic and butyric are not attacked by chromic acid. Hehner allows for variation of temperature by assuming an expansion of the dichromate solution of 0.05% per 1°. This value he found for a dichromate solution, prepared as above. Lewkowitsch avoids a temperature correction by maintaining the solutions at the normal temperature during titration by surrounding them with a large water-jacket.

Several alterations in the procedure have been suggested by Richardson and Jaffé (*J. Soc. Chem. Ind.*, 1898, **17**, 330), a stronger solution of dichromate being used and the time of boiling much reduced.

3. *Acetin Method.*—The *acetin method* of Benedikt and Cantor (*J. Soc. Chem. Ind.*, 1888, **7**, 696) depends upon the formation of triacetin (glyceryl triacetate) when glycerol is heated with acetic anhydride. The triacetin is then saponified with sodium hydroxide solution, and the amount of the latter used gives a measure of the glycerol. Lewkowitsch has shown that the method gives closely concordant results in the case of moderately pure "crude glycerins," and recommends its adoption in all cases in which the glycerol is first isolated in a fairly pure state as in its estimation in fats and oils (*v. infra*) (Lewkowitsch, *Chem. Zeit.*, 1889, **13**, 93, 191, 659; Hehner, *J. Soc. Chem. Ind.*, 1889, **8**, 6).

Solutions required:

1. N/2 or N/1 hydrochloric acid (accurately standardised).
2. Sodium hydroxide solution, 20 grm. sodium hydroxide per 1,000 c.c. Its strength need not be accurately known.
3. A 10% sodium hydroxide solution, 10%.

Solutions 2 and 3 must be kept free from the access of carbon dioxide.

Process.—1 to 1.5 grm. of the crude glycerol, 7 or 8 grm. of acetic anhydride, and about 3 grm. of anhydrous sodium acetate (previously dried in an oven) are heated from 1 to 1.5 hours in a reflux apparatus. The mixture is allowed to cool, 50 c.c. of water are added, and the heating is continued (still with the condenser, as triacetin is volatile in a current of steam) until it begins to boil. When the oily deposit at the bottom of the flask is dissolved, the liquid is filtered from a white flocculent precipitate, which contains most of the impurities of the crude glycerol, allowed to cool, phenolphthaleïn added, and dilute sodium hydroxide (No. 2 solution) run in until neutrality is obtained. Care must be taken not to pass that point, as triacetin is easily saponified.

During the operation the solution must be agitated continually, so that the acid may not be in excess locally any longer than is unavoidable. The point of neutrality is reached when the solution becomes reddish-yellow. It must not be allowed to become pink. The estimation is inaccurate if the solution is more than neutralised even for the shortest time. 25 c.c. of the strong sodium hydroxide are now added from a pipette. The mixture is then heated for 15 minutes and the excess of alkali titrated back with normal or half-normal hydrochloric acid. The strength of the alkali used is ascertained at the same time by titrating another 25 c.c. measured with the same pipette. The difference between the titrations gives the amount of alkali consumed in saponifying the acetin, and from this the quantity of glycerol is calculated.

B. Gravimetric Methods.—I. *Zeisel and Fanto's* method (*Zeit. landw. Versuchswesen Oest.*, 1902, **5**, 729). This method is based on the fact that when glycerol is boiled with an excess of hydriodic acid (sp. gr. 1.7, b. p. 127°) it is converted quantitatively into *iso*propyl iodide, which can be estimated by passing it into a solution of silver nitrate in absolute alcohol, and weighing the silver iodide formed.

$$C_3H_5(OH)_3+5HI = C_3H_7I + 3H_2O + 2I_2$$
$$C_3H_7I + AgNo_3 = AgI + C_3H_7NO_3.$$

Materials Required.—1. It is advisable to keep a stock of hydriodic acid of sp. gr. 1.9, containing 68% by weight of HI; this acid can then be suitably diluted with the aqueous glycerin or with water (3 vols. hydriodic acid to 1 vol. water), so that the acid acting on the glycerin is of sp. gr. 1.7. It must be free from sulphur and, in a blank experiment carried out as described below, give no precipitate of silver iodide in the alcoholic silver nitrate solution.

2. 40 grm. of pure silver nitrate is dissolved in 100 c.c. of water and made up to 1 litre with commercial absolute alcohol; after 24 hours the solution is filtered. The solution must be kept in the dark.

3. Red phosphorus. This must be washed with carbon disulphide, ether, alcohol, and water, and dried in the air.

The apparatus used (see Fig. 13) is a modification of the well-known Zeisel apparatus for the estimation of methoxyl. The flask, *a*, capacity 40 c.c., has a side tube attached as shown, which serves to pass carbon dioxide through the apparatus. Through the condenser, *b*, circulates water maintained at 60° ± 10° by means of an Ehmann's heating arrangement, *g*; the tube of the condenser is ground into the neck of flask, *a*, and the joint held in position by means of the small springs shown. The bulb, *c*, immersed in water at 60–70°, serves to count the bubbles of gas and is filled to about a third with a thin mixture of red phosphorus and water (a solution of potassium arsenite can be used in place of phosphorus, but the latter is preferable). The Erlenmeyer flasks, *e* and *f*, the larger with a mark showing 45 c.c., the smaller with a mark at 5 c.c., contain the clear alcoholic silver nitrate up to the marks aforesaid. The glycerin is weighed into *a*, the quantity taken being such as to give not more than 0.4 grm. of silver iodide. A fragment of pumice is introduced into *a*, 15 c.c. of the hydriodic acid (sp. gr. 1.7) added, and the flask immediately connected with the condenser and with a carbon dioxide apparatus supplying carbon dioxide, which has been washed by passing through dilute sodium carbonate solution. The carbon dioxide is passed at the rate of about 3 bubbles per second. The boiling flask is immersed in a glycerin bath so that the levels inside and outside of the flask are the same; the bath is heated by a small flame so as to keep the hydriodic acid boiling gently during the whole operation. When the liquid above the precipitated silver iodide becomes clear and the operation is complete the contents of the Erlenmeyer flasks are transferred to a large beaker; water is added so as to make a volume of 450 c.c., and then 10 to 15 drops of dilute nitrlc acid; the liquid is then

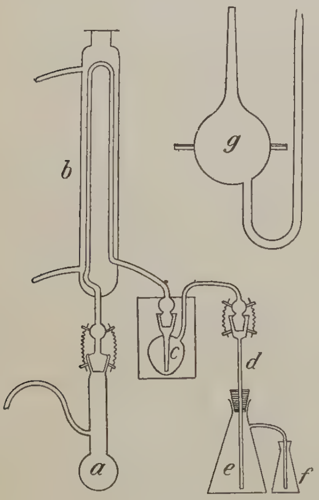

FIG. 13.

heated in a water-bath, so as to make the silver iodide readily filterable, and, on cooling, the precipitate is collected and weighed. The weight of silver iodide × 0.3920 gives the weight of glycerol present. The time of distillation varies from 2 to 4 hours; the completion of the operation is controlled by substituting for flask *e* a flask containing fresh silver nitrate solution and again distilling.

Lewkowitsch (*Analyst*, 1903, **28**, 108) states that the above method does not give accurate results for crude glycerin on account of the presence of impurities in the latter. Other workers, however, highly commend it (Schuch, *Ztsch. für landw. Versuchswesen Oest.*, 1904, **7**, 111; Hertmann, *Beiträge z. chem. Physiologie u. Pathologie*, **5**, 422). From a very detailed comparative study of the different methods of estimating glycerol, Schulze (*vide infra*) has concluded that the Zeisel-Fanto method is the most accurate under all conditions of all the methods yet devised for estimating glycerol.

Instead of the special apparatus described by Zeisel and Fanto, a modification of Perkin's form of the ordinary Zeisel apparatus would probably prove more simple in use.

II. *Shukoff and Schestakoff's Method* (*Zeit. angew. Chem.*, 1905, **18**, 294).—This is a direct method, based on the fact that on mixing a glycerol solution with sodium sulphate dehydrated by ignition and extracting the mass with acetone the whole of the glycerol passes into solution. As the method is tedious, and in many cases gives values as much as 1% in error (compare Landsberger, *Chem. Rev. Fett u. Harz. Ind.*, 1905, **12**, 150; Dynamitfabrik Schlebusch, *Zeit. angew. Chem.*, 1905, **18**, 1656), it will not be described here.

C. Physical Methods.—When occurring in admixture with water only, the proportion of glycerol is most easily deduced from the sp. gr. or from the index of refraction of the liquid. The tables on pages 448–450 give the values of these constants for different strengths of solution. The values obtained by Lenz (at 12 to 14°) are probably the most reliable.

Sp. Gr.—The sp. gr. of solutions of glycerol cannot be accurately measured by the hydrometer, the values obtained being 0.002 to 0.003 too high. If a Sprengel tube is used it is filled by means of an air-pump with the glycerol which has previously been heated in a closed flask on the water-bath so as to diminish the viscosity. The tube is then immersed in water at one of the following temperatures: 12 to 14° (Lenz), 15°, 15.5 or 20°. If a pyknometer is used (Lewkowitsch), the following precautions have to be taken:

The sample is warmed in a closed bottle by immersing in warm water until all air-bubbles have collected at the top. The glycerol is then allowed to cool in the cooled bottle, preferably to the normal temperature, and then carefully filled into the pyknometer provided with a perforated stopper. If this has been pushed home, after the last filling, the very small drop of glycerol squeezed out is wiped off with a linen cloth and the bottle taken out of the water-bath. The determination may be made exact to the fourth decimal if the weights are reduced to vacuum. Complicated calculation is avoided by ascertaining once for all the necessary corrections for the pyknometer when filled with water. Suppose the weight p has been found in air, then the corrected weight P will be:

$$P=p+pR.$$

For brass weights, the correction R for the sp. gr. likely to occur is found from the following table:

Sp. gr.	Correction (R)	Sp. gr.	Correction (R)
1.00	0.00106	1.10	0.00095
1.02	0.00103	1.15	0.00090
1.04	0.00101	1.20	0.00086
1.06	0.00099	1.25	0.00082
1.08	0.00097	1.30	0.00078

If the temperature is not one of those corresponding with the tables on page 448, a correction of 0.00058 may be made for each 1° difference of temperature. Lenz's values at 12 to 14° have been calculated to 15.5° by Richmond using this factor: The following table shows the result.

Percentage	Sp. gr. at 15.5°	Percentage	Sp. gr. at 15.5°
100	1.2674	87	1.2327
99	1.2647	86	1.2301
98	1.2620	85	1.2274
97	1.2594	84	1.2248
96	1.2567	83	1.2222
95	1.2540	82	1.2196
94	1.2513	81	1.2169
93	1.2486	80	1.2143
92	1.2460	79	1.2117
91	1.2433	78	1.2090
90	1.2406	77	1.2064
89	1.2380	76	1.2037
88	1.2353	75	1.2011

Refractive Index.—This is ascertained by one of the many forms of refractometer. In order to avoid the necessity of maintaining a known constant temperature and of accurately ascertaining the zero error of the instrument, Lenz recommends that the refractive index of the glycerol solution and of pure water be observed successively. The following table gives the differences between the refractive index of water and of aqueous solution of glycerol of different concentrations.

TABLE OF DIFFERENCES BETWEEN REFRACTIVE INDICES OF AQUEOUS SOLUTIONS OF GLYCEROL AND OF PURE WATER. (N_D SOLUTION—N_D WATER) (LENZ).

% glycerol	Difference	% glycerol	Difference	% glycerol	Difference	% glycerol	Difference	% glycerol	Difference
100	0.1424	80	0.1133	60	0.0806	40	0.0526	20	0.0261
99	0.1410	79	0.1119	59	0.0792	39	0.0510	19	0.0238
98	0.1395	78	0.1104	58	0.0780	38	0.0495	18	0.0225
97	0.1381	77	0.1090	57	0.0768	37	0.0479	17	0.0212
96	0.1366	76	0.1075	56	0.0757	36	0.0464	16	0.0199
95	0.1352	75	0.1061	55	0.0745	35	0.0451	15	0.0186
94	0.1337	74	0.1046	54	0.0731	34	0.0438	14	0.0173
93	0.1323	73	0.1032	53	0.0717	33	0.0424	13	0.0160
92	0.1308	72	0.1018	52	0.0702	32	0.0411	12	0.0146
91	0.1294	71	0.1003	51	0.0688	31	0.0398	11	0.0133
90	0.1279	70	0.0987	50	0.0663	30	0.0385	10	0.0120
89	0.1264	69	0.0970	49	0.0659	29	0.0372	9	0.0108
88	0.1250	68	0.0952	48	0.0645	28	0.0358	8	0.0096
87	0.1235	67	0.0933	47	0.0630	27	0.0345	7	0.0083
86	0.1221	66	0.0915	46	0.0616	26	0.0332	6	0.0071
85	0.1206	65	0.0897	45	0.0601	25	0.0318	5	0.0058
84	0.1191	64	0.0889	44	0.0587	24	0.0315	4	0.0046
83	0.1177	63	0.0861	43	0.0572	23	0.0302	3	0.0033
82	0.1162	62	0.0842	42	0.0556	22	0.0288	2	0.0021
81	0.1148	61	0.0824	41	0.0541	21	0.0275	1	0.0008

Degree of Accuracy of Different Methods for Estimating Glycerol.—F. Schulze (*Chem. Zeit.*, 1905, **29**, 976) has recently made a systematic comparison of the methods in use for estimating glycerol; he gives tables showing the results obtained with fats, soaps, and various commercial glycerins. The following are his principal conclusions:

1. The permanganate method is considered unreliable in all cases, whether carried out by the method of Benedikt and Zsigmondy, or by Herbig or Mangold's modifications.

2. The acetin method failed to give concordant results. If this method is still to be employed, it is essential that the mean of several estimations be taken.

3. The dichromate method gives high results as a rule. Approximate values may be obtained by lowering the figures obtained by 10%. The method is valid only in absence of phosphoric acid.

4. Zeisel and Fanto's method is regarded as the most accurate for scientific and general purposes, but it is too expensive for ordinary factory working. In such cases it should be used as a check on the dichromate method.

Lewkowitsch (*ChemicalTechnology of Fats and Oils*) considers that for ascertaining the proportion of glycerol in its *pure* dilute aqueous solution, oxidation methods are best, and that either the permanganate or dichromate method gives good results in such cases. On the other hand, there is no doubt that such methods give high results with impure glycerin. In such cases the acetin method is preferred. The Zeisel-Fanto method is said by Lewkowitsch not to give good results.

Physical methods can, of course, be expected to give accurate results only with aqueous solutions of pure glycerol; in presence of a known proportion of known salts, the influence of the latter on the physical properties can, however, be calculated. Several methods have been proposed for estimating the approximate proportion of glycerol in crude glycerin by making an allowance of this kind (compare for example, Richardson and Jaffé, *loc. cit.*; Stiefel, *Seifensiederzeitung*, 1905, **31**, 818), but the results obtained can only be regarded as approximations.

COMMERCIAL "GLYCERIN."

Three kinds of "glycerin" call for consideration: 1. Crude glycerin; 2. distilled or dynamite glycerin; 3. chemically pure glycerin.

1. CRUDE GLYCERIN.

Three kinds of crude glycerin may be distinguished: Saponification glycerin, distillation glycerin, soap-lye glycerin or soap glycerin.

Saponification Glycerin.—This glycerin is obtained by the autoclave process of hydrolysing fats by heating with water under high pressure, either alone or in presence of a small proportion of lime or magnesia. It is evaporated to a sp. gr. 1.240–1.242, and is then known as "28° B.," "*raw glycerin*," "*saponification glycerin* or "*candle glycerin*." It has a sweet taste, and varies in colour from bright yellow to dark brown. It gives but a slight precipitate with basic lead acetate, and with hydrochloric acid should give no turbidity. The valuation of such glycerin includes the estimation of glycerol, ash (which should not exceed 0.3 to 0.5%), and organic impurities.

Glycerol.—Lewkowitsch recommends the acetin method for this purpose. Of the oxidation methods only that of Hehner is available, and this (*Analyst*, 1903, **28,** 104) gives high results. The % of glycerol varies in saponification glycerin from 85 to 90%.

Organic Impurities.—The glycerol is volatilised off by heating several grm. of the sample in a platinum dish *gradually* to 160°. Rapid heating gives rise to non-volatile polyglycerols, and the result is found too high. During the heating the mass is best moistened with a few drops of water so that the glycerin volatilises in steam. The product is dried to constant weight. The amount of *ash* is then ascertained by ignition. The difference in weight gives the organic impurities.

Distillation Glycerin.—This is obtained from the waste acid liquors obtained in the acid hydrolyses (or saponification) of fats. It is evaporated to a sp. gr. 1.240 to 1.242 and then has a disagreeable odour when rubbed on the hand, a sharp astringent taste and a bright yellow colour. It generally contains 84 to 86% glycerol; the ash is high (2 to 3.5%). This glycerin gives a heavy precipitate with lead acetate and a decided turbidity (fatty acids) on adding hydrochloric acid. Lewkowitsch recommends the acetin method for estimating glycerol.

Soap-lye Glycerin.—This is obtained from spent lyes. The sp. gr. should not fall below 1.3 mm., the percentage of glycerol below 80. The ash may be as high as 10% and consists in good samples, mainly of common salt. The glycerol is best estimated by the acetin method.

Ash.—3–5 grm. are cautiously heated in a platinum dish over a small flame. The glycerol is first driven off so as to leave a voluminous residue of carbon in the dish; the residue is then more strongly heated so as to char all organic substances, but not sufficiently to volatilise the common salt. The carbonaceous residue is then extracted with water, the solution filtered and evaporated in the platinum dish on the water-bath. The residue, which must be white, is heated gently (not above 400°) and weighed (Lewkowitsch). The carbon on the filter may, as a rule, be disregarded unless a large proportion of lime is present, when it is burnt away.

The weight of the ash having been ascertained, it may be further examined for lead, iron, zinc, magnesium, calcium carbonates, chlorides, sulphates, etc. The ash is treated with dilute sulphuric acid, when the *copper*, *iron*, *zinc*, *magnesium*, and more or less *calcium* will be dissolved as sulphates, and can be detected in the solution by the usual methods. The residue will contain lead sulphate, together, possibly, with calcium sulphate. On treating it with a hot solution of ammonium acetate, the lead sulphate will be dissolved, and the resultant solution will give a yellow precipitate with potassium chromate and a black precipitate with hydrogen sulphide.

Calcium is a frequent impurity occurring most commonly as calcium oleate. It is most readily estimated by precipitating the diluted sample with ammonium oxalate. Precipitation in an alcoholic solution with sulphuric acid has been recommended by Cap, but presents no advantages over the oxalate method.

Alkalinity in commercial glycerol is due almost entirely to sodium carbonate, and is readily estimated by titrating the diluted sample with standard acid. Sulman and Berry recommend the use of litmus as an indicator, neither phenolphthaleïn nor methyl-orange giving sharp end-points. Glycerin from soap-lyes is purposely alkaline, owing to the risk of concentrating it in presence of acid. The alkalinity usually varies from 0.5 to 2.0%, depending to some extent on the manner in which the lyes have been treated. In a case cited by Fleming, in which the glycerin had been separated from the lye by alkali instead of salt, the resulting glycerin contained 31% of sodium carbonate.

Chlorides cannot be estimated by direct titration or precipitation with silver, owing to the solubility of silver chloride in glycerol and the reduction of the nitrate by various impurities. The estimation is best made by allowing a weighed portion to burn away as already described, exhausting the carbonaceous residue with water, and titrating the filtered solution with N/10 silver nitrate, using neutral potassium chromate as an indicator. Crude soap-lye glycerins usually contain from 5 to 10% of salt.

Sulphates may be estimated by precipitating the diluted sample with barium chloride. They are usually present in the product from soap-lyes, and sometimes in very large amount. Glycerins obtained by saponifying fat with sulphuric acid are always charged with sulphates and often contain *sulphites*, *thiosulphates* and *sulphides*, the last three being objectionable. The milky precipitate produced on acidifying the raw product from soap-lyes sometimes contains a considerable proportion of free *sulphur*, the proportion amounting in some cases to

40 or even 60% of the whole precipitate. Such samples will yield objectionable volatile sulphur compounds on distillation.

C. Ferrier (*Chem. Zeit.*, 1893, **16**, 1840) proposes the following method for detecting sulphur compounds: The sample is diluted with 10 times its volume of water and neutralised with hydrochloric acid. This mixture is treated at from 60° to 70° with about 3% of the carbon residue from the manufacture of potassium ferrocyanide (which has been previously washed with dilute nitric acid and water and heated to redness in a closed crucible). One drop of the solution after treatment with the purified carbon residue is placed on a strip of paper saturated with lead nitrate. If no yellow stain appears, the sample contains less than 0.0001 part of sulphides. To detect a still smaller quantity, the sample is heated in a small flask with a few drops of hydrochloric acid and a little sodium carbonate held over the mouth of the flask.

To detect *thiosulphates* and *sulphites* a few c.c. of barium chloride solution are added to the solution of the sample and the liquid filtered. Barium sulphite is precipitated and the thiosulphates may be found in the filtrate, which, on addition of potassium permanganate to the acidified solution, will become cloudy, even in the presence of only 0.0001 part of thiosulphate.

The presence of sulphite in the precipitate is proved by washing it repeatedly with boiling water, then adding to the remaining precipitate a few drops of starch and iodine solution; in presence of sulphites the blue will gradually disappear. See also Richardson and Aykroyd (*J. Soc. Chem. Ind.*, 1896, **15**, 171) for the quantitative estimation of these compounds.

Organic impurities are estimated in soap-lye glycerin just as in saponification glycerin.

Protein matter, derived from the envelopes of the fat globules, is nearly always present to a greater or less extent, the product from soap-lyes containing the largest proportion, owing to the solvent action of the alkali on the proteid matter of the fats saponified. They are objectionable on account of the mechanical difficulties they occasion during the subsequent distillation, and the contamination of the distillate with empyreumatic and coloured products. An approximate estimation of the protein matters may be made by precipitating with basic lead acetate, and applying the Kjeldahl method. The nitrogen, multiplied by 6.25, gives the amount of protein in the precipitate.

Rosin is a very frequent and objectionable impurity in the glycerin from soap-lyes, but is absent from that from candle-works. A portion of the rosin is precipitated on acidifying, but the use of basic lead acetate is better. When rosin is present, the distillate often has a strongly-marked fluorescence from the presence of rosin oil. This impurity may be further detected and removed by agitating the sample with ether or petroleum spirit, which, after separation and evaporation, leaves the rosin oil in a form recognisable by its physical characters, taste, and odour on heating.

Higher fatty acids, chiefly *oleic acid*, are not unfrequently present in glycerin from soap-lyes, even after distillation, and are very objectionable in a product intended for making nitroglycerin (*v. infra*). If the amount of fatty acids be considerable, mere dilution with water causes their precipitation, but smaller quantities may be detected by diluting the glycerol and passing nitrogen dioxide (NO_2) through the sample, when a flocculent precipitate of elaïdic acid (less soluble than the original oleic acid) will be produced. Nitrogen dioxide is best obtained by heating dry lead nitrate in a tube or small retort.

Fatty acids may be detected by diluting a portion of the sample with several times its bulk of water and acidifying with hydrochloric acid. In the presence of fatty acids the liquid becomes turbid.

By agitating glycerin with chloroform, fatty acids, rosin oil, and some other impurities are dissolved, while certain others form a turbid layer between the chloroform and the supernatant liquid. On separating the chloroform and evaporating it to dryness, a residue is obtained which may be further examined.

Lower fatty acids, especially butyric and formic acids, may be not unfrequently present. The presence of free oxalic, formic, or butyric acid in distilled glycerol will be indicated by the acid indication of the sample, and an estimate of the amount present can be obtained by titrating the diluted sample with standard alkali and litmus or phenolphthaleïn. *Butyric acid* is sometimes present to the extent of 0.5% of the fats saponified. Samples containing it develop an odour of sweat when mixed with a few drops of dilute sulphuric acid and rubbed between the hands. *Formic acid*, traces of which are often present even in distilled glycerol, is best detected by adding ammoniacal silver nitrate to the diluted sample. On leaving the mixture at the ordinary temperature for half an hour, a black precipitate will be produced if formic acid be present. After a longer interval, all samples of commercial glycerol cause a reduction of ammoniacal silver nitrate, at least, if the liquid be exposed to light; and at temperatures above 50° the change occurs with greater facility.

The presence of *formic* and *butyric acids* may be confirmed by gently heating the sample with alcohol and strong sulphuric acid, when esters of agreeable and characteristic odour will be formed. Ethyl formate has an odour of peaches, and ethyl butyrate that of pineapple.

With a neutral solution of silver nitrate, pure diluted glycerol gives no precipitate. In presence of *formic acid*, *butyric acid*, or *acroleïn*, a white precipitate is formed, which blackens on standing or boiling. French perfumers and manufacturers of cosmetics reject samples which show any change of colour or turbidity within 24 hours after the addition of silver nitrate. Sulman and Berry found that nearly all commercial samples in bulk speedily effected reduction of the silver, with consequent blackening of the precipitate previously formed. *Nitric acid* has been found in distilled glycerol. Its presence, which cannot have been due to accident, masks the test with silver nitrate, and prevents the detection of impurities which are very objectionable in material intended for nitrating.

2. DISTILLED AND DYNAMITE GLYCERIN.

Distilled glycerin is obtained by distilling crude glycerin. It varies in colour from yellow to nearly white, and contains an amount of glycerol depending on its sp. gr., which varies from 1.22 to 1.26; the percentage of glycerol is very approximately obtained from the sp. gr. To obtain a more accurate value, the acetin method is recommended by Lewkowitsch; oxidation methods give high results (*v. infra*).

Dynamite glycerin is the name given in the trade to distilled glycerin having a sp. gr. 1.261 or above. Its colour varies from deep yellow to bright straw-yellow. Lewkowitsch collects from a number of buyer's specifications the following points as characteristics of good dynamite glycerin.

(*a*) *Sp. gr.* must not be less than 1.261 at 15.5°.

(*b*) *Lime, magnesia,* and *alumina* must be absent.

(*c*) *Chlorides* must be present only as traces. When to 1 c.c. of glycerin diluted with 2 c.c. of water silver nitrate is added only a faint turbidity should be produced.

(*d*) *Arsenic.*—Only traces are permissible. The Gutzeit test being too delicate, the following should be used. The glycerin is made *very* faintly alkaline by the addition of the least possible quantity of ammonia; on adding silver nitrate no milkiness should be visible. An excess of ammonia must be avoided as silver arsenite is soluble in ammonia.

(*e*) *Organic Impurities.*—1 c.c. of the sample is diluted with 2 c.c. of water and mixed with a 10% solution of silver nitrate. The liquid should not become black or brownish within 10 minutes.

(*f*) *Total non-volatile residue*—ascertained as on page 467. It should not exceed 0.15%.

(*g*) *Free Acid.*—The glycerin must not redden blue litmus-paper. Volatile fatty acids are detected by the production of a fruity odour (ester formation) when the sample is heated with alcohol and concentrated sulphuric acid. 1 c.c. diluted with 2 c.c. of water should give no precipitate on adding strong hydrochloric acid.

It may often happen that a sample which will answer the above requirements is yet unsuitable for the manufacture of dynamite; it must, therefore, be nitrated in the following way, which imitates the conditions obtaining on the large scale. A mixture of 1 part by weight of fuming nitric acid (sp. gr. 1.5) and 2 parts of pure sulphuric acid (1.845) is prepared, and allowed to cool in a stoppered vessel. 375 grm. of the mixed acid are put into a thin-walled beaker of about 500 c.c. capacity, and stood in a large vessel through which a constant current of cold water passes. Great care must be taken that the water does not splash into the beaker, to which end the leading tube should be firmly fixed both to the tap and the basin. 50 grm. of the glycerin are weighed out, and, when the acids are not hotter than from 12° to 15°, added *drop by drop*, using a thermometer as a stirrer. The stirring must be very thorough to avoid local heating, and the temperature must not be allowed to rise to 30°, 25° being a safer limit. It the temperature indicates danger, the bottom of the beaker should be instantly perforated with the thermometer. The small beaker may be weighed again to give the exact amount of the sample added, and when the temperature of the other has fallen to 15°, the liquid is run out into a perfectly dry separating funnel, which may advisedly receive a preliminary rinse with strong sulphuric acid. The quicker the separation of the liquids, and the sharper the line of demarcation between the nitroglycerin and the acids, the better is the glycerin. The nitroglycerin is always slightly turbid, but if it contains flocks, or the separation is not complete in 5 or 10 minutes, or if there is a cloudy middle layer of liquid, the glycerin must be rejected. With very bad samples, no separation at all may be obtained on standing several hours.

If it is desired to make the test quantitative, the operation may be continued. The acids are run off; the nitroglycerin carefully swung round in the separator to detach drops of acid from the walls (without shaking it, however), and after these drops are removed, washed with warm (35° to 40°) water, once or twice with 20% sodium hydroxide solution, and again with water. It is then run into a 100 c.c. burette, or graduated tube, and when the excess of water has risen to the top, the volume read off. This, multiplied by 1.6, gives its weight, and the yield should be at least from 207 to 210%—the higher the better (theory requires 246.7). If preferred, it may be weighed directly after filtration over salt, and its sp. gr. taken. The loss in the wash-waters is insignificant.

To destroy the nitroglycerin, it is best absorbed in a thin layer of sawdust spread in an open yard removed from any buildings, and then set on fire with a match. It will burn away quietly.

Owing to the danger attending this test, many chemists diminish the quantity of sample used to 15 grm. This is the smallest quantity that should be taken, as with less than this amount the test is quite useless.

3. PURE GLYCERIN.

Chemically pure glycerin comes on the market in three grades: sp. gr. 1.24, sp. gr. 1.25, sp. gr. 1.26, respectively. The "glycerinum" of the British Pharmacopœia has a sp. gr. 1.26; that of the United States Pharmacopœia of 1.25.

The percentage of glycerol in pure glycerin can be ascertained by taking the sp. gr. on observing the refractive index in the manner already described (page 465). With dilute solutions the percentage of glycerol is best ascertained by means of the dichromate method; Lewkowitsch also recommends the permanganate method for this purpose (compare above.)

Ash plus polyglycerins should not exceed 0.03%; *ash* alone should not exceed 0.01%.

Acrolein (and other reducing substances) are best detected by adding a few drops of silver nitrate solution to the diluted glycerin; after standing 24 hours there should be no visible blackening. The test is made more sensitive by using ammoniacal silver nitrate.

Volatile fatty acids are detected as on page 470.

Arsenic must not exceed 1 part in 250,000. The best test for arsenic is the Gutzeit test, which is carried out as follows:

Place in a tall test-tube about a grm. of pure zinc, 5 c.c. of diluted sulphuric acid (6%), and 2 c.c. of the sample. The mouth of the test-tube is then covered with a tightly-fitting cap, made of 3 thicknesses of filter-paper. A drop of a 50% solution of silver nitrate is placed on the inner surface layer and the tube allowed to stand for 10 minutes in the dark. If arsenic is present, a bright yellow stain will appear on the filter-paper, which, on the addition of water, becomes black or brown. A blank test should always be made to establish the absence of arsenic in the reagents. Sulphides (which may be detected by substituting lead acetate for the silver nitrate in the above test) must be oxidised to sulphates before applying the test.

The test is extremely sensitive. A less rigorous test may be made by substituting a drop of a saturated solution of mercuric chloride for the silver nitrate. If no yellow colouration appears after 10 minutes, the sample may be considered free from arsenic.

Pure glycerol does not acquire a yellow or brown colour when very gradually mixed with an equal volume of cold concentrated sulphuric acid. Sugar and certain other impurities cause a marked darkening, or even charring, and in presence of any considerable quantity of formic or oxalic acid the mixture effervesces when warmed. *Oxalic acid* may be recognised more certainly by the formation of a white turbidity on adding calcium acetate to the diluted sample. It is not unfrequently present in raw, but never in distilled samples.

Pure dilute glycerol does not sensibly reduce Fehling's solution when heated with it to 100° for a few minutes, but prolonged boiling causes precipitation of cuprous oxide. Dextrose and arsenious acid will reduce the solution even before the b. p. is reached. Arsenic occurs in glycerin recovered from soap-lyes which have been neutralised by crude hydrochloric acid, owing to the fact that it volatilises (probably as a compound of glycerol) when the glycerol is distilled. *Cane-sugar* can be recognised by the same test, if the sample is previously heated to 70° or 80° for 10 minutes in 5 times its volume of water and half its volume of strong hydrochloric acid, and the inverted solution be neutralised with sodium hydroxide before adding the cupric solution. The test can be made quantitative if proper precautions be taken (see Vol. 1). Cane-sugar will be further indicated by the charring produced on mixing the sample with strong sulphuric acid, and warming; and dextrose by the brown colouration produced on boiling the sample with a solution of sodium hydroxide. Dextrose may further be recognised by the reduction which ensues on heating the diluted glycerin to 70° with potassium ferricyanide and potassium hydroxide. On acidifying the solution and adding ferric chloride, prussian blue will be formed if dextrose was originally present.

Cane-sugar, dextrose, and dextrin (but not milk-sugar or arabin) may also be recognised by a test due to Mason. A mixture of 0.5 c.c. of the sample, 15 c.c. of water, 2 drops of strong nitric acid (not more), and 0.5 grm. of ammonium molybdate is boiled for 2 or 3 minutes, or longer if the quantity is small, when a blue colouration will be produced if 0.25% or more of one of the above impurities be present. Dextrin and gum would also be precipitated on diluting the sample with a large proportion of alcohol. They may be distinguished as described in Vol. 1.

Sugar and other carbohydrates may also be detected and estimated by observing the optical activity of the samples (see Vol. 1). They can occur only as adulterants. Lajoux (*Chem. Zeit.*, 1882, **6**, 1035) states that a saturated solution of magnesium sulphate mixed with commercial glucose has been used in France as an adulterant for glycerol.

The analysis of mixtures of sugar and glycerol has been already described (Method of Donath and Mayrhofer). If the actual separation of the substances for gravimetric estimation or subsequent examination is desired, the best plan is to separate other organic compounds as far as possible by precipitating the cold solution with basic lead acetate used in slight excess, concentrate the filtrate at a low temperature, and extract the residue with a mixture of 2 volumes of absolute alcohol and 1 of ether, or of 2 of alcohol and 1 of chloroform. These solvents leave the sugar undissolved, while the glycerol contained in the solution can be recovered more or less completely by evaporating the solution at a low temperature. If the solution be diluted with about twice its measure of water and faintly acidified before evaporating, the layer of ether or chloroform which separates often carries with it much of the colouring matter and resinous impurities which may be present, thus leaving the glycerol in a comparatively pure form.

Distinction Between Raw and Distilled or Pure Glycerin.—The values found for ash, organic impurities, and the difference in behaviour with basic lead acetate give a means of distinguishing between distilled and undistilled glycerin.

All so-called crude glycerin imported into the United States is examined by the government chemists to ascertain whether it is really crude or has been partially or wholly refined, as in the latter case a higher rate of duty is charged. Glycerin that has been freed from impurities by allowing them to subside and then straining and filtering, is still classed as "crude," but if proved to have been subjected to further purification it is classed as "refined." For practical purposes of classification distillation is regarded as the dividing line between crude and refined glycerin. For this purpose J. H. Wainwright (*J. Soc. Chem. Ind.*, 1889, **11**, 125) attaches great importance to the following tests:

The *Carbonaceous Residue* is obtained by heating 10 grm. of the sample in a platinum crucible till it ignites, when the source of heat is removed and the sample is allowed to burn away spontaneously. In distilled glycerin this will not be over 0.5%. Crude glycerin may yield as much as 10%. The percentage of ash appears to be a less reliable criterion, but should not be over 0.1%.

Silver Nitrate Test.—5 c.c. of the sample are diluted with 20 c.c. of distilled water, mixed with 5 c.c. of a 2% solution of silver nitrate, and allowed to stand for one hour. Only a slight precipitate will be formed with distilled glycerin at the end of this time; whereas with crude glycerin the precipitate is large, usually comes down at once, and is almost always *flocculent.*

Lead Test.—The solution is prepared by boiling 10 grm. of lead acetate and 8 grm. of lead oxide with 500 c.c. of water, and filtering. 2 volumes of this solution are mixed with 1 volume of glycerin and 1 of distilled water, and allowed to stand for 1 hour. Refined glycerin may produce a slight precipitate, but this is never *flocculent.* Crude samples produce a more or less abundant flocculent precipitate.

Wainright does not consider it safe to rely upon either of the two last-mentioned tests alone, but if a sample will not stand both of them, it is thought perfectly safe to call it crude.

Mr. Chas. C. Roberts, of the United States Customs Laboratory at Philadelphia, furnishes the information that these tests are still in use, and in addition refined glycerin should give only inappreciable precipitates with ammonium oxalate and barium chloride, the sample being diluted as noted above. The reaction should be neutral or slightly acid, and the sp. gr. at 15.6°, 1.2500. The sp. gr. is not, however, regarded by the appraisers as an absolute requirement. Samples not according with these requirements for "refined glycerin" are dutiable as "crude."

Estimation of Glycerol in Special Cases.

1. In **beer, spirits and wine** (see the sections on these subjects in Vol. 1).

2. In **oils and fats:** The estimation of glycerol in the glycerides present in fats and oils is generally carried out by the acetin method. 20 grm. of the fat or oil are saponified with alcoholic potassium hydroxide as in determining the Reichert value (page 22). The soap is dissolved in a considerable volume of water, and decomposed with dilute sulphuric acid; the precipitated fatty acids are filtered off, an excess of barium carbonate is added to the filtrate which is then evaporated on the water-bath until most of the water has been driven off. The residue is then extracted with a mixture of ether and alcohol (1:3), the bulk of the ether-alcohol volatilised carefully on the water-bath and the residue dried in a desiccator (preferably in a vacuum) and weighed. It is not necessary to dry the glycerin to a constant weight, as the amount of glycerol in it is determined by means of the acetin method described on page 460, taking 1 to 1.5 grm. of the crude glycerin for the experiment.

Fanto's Method (*Zeit. angew. Chem.*, 1904, **17**, 420).—10 grm. of the sample are saponified with 100 c.c. of N/2 alcoholic potassium hydroxide, the alcohol is partly evaporated, 100 c.c. of water is added, and the fatty acids liberated by adding acetic acid. The mixture is then cooled, and the solid fatty acids which separate are collected on a filter and thoroughly washed about 5 times with 15 to 20 c.c. of boiling water; if the fatty acids are liquid it is advisable to add a little paraffin wax to accelerate solidification. The aqueous filtrate and washings are boiled down to about 60 c.c., and when cold made up to 100 c.c. in a measuring flask. 5 c.c. is then taken for the estimation of glycerol by Zeisel and Fanto's method (see page 461).

Lewkowitsch (*Analyst*, 1903, **28**, 104) found that Zeisel and Fanto's method gave incorrect results when the fat was treated directly with hydriodic acid; the modification described above of the original method is stated by Fanto to be quite accurate. Schulze, as already stated, prefers Fanto's method to all others.

3. **Glycerol in Soap.**—See under Soap.

4. **Glycerol in Soap-lyes.**—A known quantity of soap-lyes is concentrated so as to give a crude glycerin and the percentage of glycerol in this estimated by the acetin method (Lewkowitsch).

Fanto recommends (*Zeit. angew. Chem.*, 1903, **16,** 413) the following modifications of Zeisel and Fanto's method described above.

20 c.c. of the lye are diluted with 2 to 3 volumes of water and an amount of silver sulphate added equivalent to the chlorides present. After warming on the water-bath during several minutes, shaking well at intervals, a hot solution of barium chloride is added so as to precipitate the whole of the sulphuric acid. The liquid is filtered, the precipitate thoroughly washed with hot water, and the filtrate and washings evaporated to 80 c.c. After cooling the liquid is made up to 100 c.c., and the glycerol in 5 c.c. estimated by the hydriodic acid method.

CHOLESTEROL AND PHYTOSTEROL.

By JOHN ADDYMAN GARDNER, M. A., F. I. C.

CHOLESTEROL. CHOLESTERYL ALCOHOL.

$C_{27}H_{46}O = C_{27}H_{45}OH$.

Cholesterol is widely distributed in the animal kingdom, but has never been found in the vegetable kingdom. It is present in bile, blood-corpuscles, blood serum, brain, spinal cord, sperm, yolk of egg, perspiration, and skin grease; in the glands—liver, kidney, pancreas, salivary, stomach, and ovaries; in the fat tissues—bone-marrow, under-skin fat, kidney fat, milk fat; in tendons and muscles. It occurs also in the tissues of the lower animals and has been recently found in various species of sea anemone (*Actinia equina* and *Taclia crassicornis*) (Dorée, *Biochemical Journal*, 1909, 4, 72. It is found in most pathological fluids and tumours, gall-stones often containing as much as 98% of their weight of cholesterol. There can be no doubt that it is a constant constituent of all killed animal protoplasm.

Cholesterol is quite insoluble in water, very slightly soluble in cold dilute alcohol, still less so if the alcohol contains salt in solution. It is easily soluble in 5 to 9 parts of boiling alcohol, in 3.7 parts of ether, 6.6 parts of chloroform, and in acetone, benzene, petroleum ether, carbon disulphide, and turpentine. It is also dissolved by volatile and fatty oils and by aqueous solutions of bile salts. It crystallises from ether or chloroform in anhydrous silky needles, and from 80 to 90% alcohol in characteristic rhombic plates containing $1H_2O$. It loses this water at 100° or in a vacuum. Anhydrous cholesterol melts at 147° and has a sp. gr. 1.046. It is lævorotatory, and the specific rotatory power appears to be independent of temperature and strength of solution and is not altered even by long standing. In ether solution $(\alpha)_D = -31.12°$, but in chloroform $(\alpha)^{16}_D = -36.61°$. On heating, it sublimes almost without decomposition in delicate laminæ and can be distilled *in vacuo*.

Cholesterol is not acted on by dilute acids, or by concentrated alkaline solutions even on boiling. Lewkowitsch has noted that when cholesterol is heated with soda-lime no, or at most very small quantities of fatty acids are formed—an important difference from aliphatic alcohols. Chemically, cholesterol behaves as an unsaturated secondary alcohol.

Cholesterol dibromide, $C_{27}H_{46}Br_2O$, is best prepared by dissolving 50 grm. of cholesterol in 500 c.c. of ether and adding a solution of 25 grm. of bromine in 250 c.c. of glacial acetic acid. After a short time the mixture sets to a mass of crystalline needles of cholesterol dibromide. These are filtered on the pump, washed with acetic acid and then with water. The dibromide thus prepared is pure, and if the small quantity that remains in solution is precipitated by the addition of water the yield is quantitative.

The dibromides of the esters of cholesterol may be prepared in a similar manner. Cholesterol dibromide prepared as above melts at 123°. It is readily reduced to cholesterol by the action of zinc dust and glacial acetic acid or of sodium amalgam in presence of ether.

The calculated iodine-absorption of cholesterol is 68.3. Lewkowitsch obtained figures closely approximating to this.

Cholesteryl Esters.—*Cholesteryl acetate*, $C_{27}H_{45}C_2H_3O_2$, is best prepared by boiling cholesterol for 20 to 30 minutes with an excess of acetic anhydride. It crystallises from benzene in needles. It is fairly soluble in ether and slightly so in cold alcohol, but more readily in hot. It melts at 113°, and has a specific rotatory power. $(\alpha)_D = -29.8°$.

Cholesteryl propionate, $C_{27}H_{45}C_3H_5O_2$, is prepared by heating anhydrous cholesterol with half its weight of propionic anhydride on the water-bath for half an hour. On cooling, the propionate separates as a white mass, and may be purified by repeatedly dissolving in ether and reprecipating with alcohol. It crystallises in rhombic plates something like cholesterol, and melts at 98°. On cooling from the melted state a play of colours is seen about the point of solidification—violet, blue, green, orange, copper-red by reflected light and the complementary colours by transmitted light. This is very characteristic.

Cholesteryl benzoate, $C_{27}H_{45}.C_7H_5O_2$, is formed by heating cholesterol with benzoyl chloride or benzoic anhydride, but the best way to prepare it is to dissolve cholesterol in dry pyridine and add a moderate excess of benzoyl chloride. The mixture is allowed to stand overnight, and then poured into water. The precipitated cholesteryl benzoate is washed with a little alcohol and recrystallised from ethyl acetate or from boiling alcohol. It is only slightly soluble in absolute alcohol. If crystallized from alcohol, the mother liquors retain at 20° 0.12 grm. per 100 c.c. The crystals are, however, more difficultly soluble. The writer found that on allowing crystals to stand in alcohol at 20° for several hours with occasional shaking only 0.029 grm. dissolved in 100 c.c. Cholesteryl benzoate melts at 145 to 146° to a turbid liquid, which becomes clear at 178°. On cooling from 178°, an azure-blue colour appears, and this changes to a deep blue colour at about the point of solidification, which persists for a few moments. This behaviour is exceedingly characteristic.

Cholesteryl chloride, $C_{27}H_{45}Cl$, was first obtained by Berthelot by heating cholesterol at 100° with strong hydrochloric acid for 10 hours. It may also be prepared by the action of phosphorus pentachloride on cholesterol, but, according to Diels and Abderhalden, it is most readily obtained by the action of thionyl chloride. Cholesterol dissolves in this substance with foaming and the solution eventually sets to a stiff mass of cholesteryl chloride, which may be purified by crystallisation from ether. It melts at 96°, and has a specific rotatory power $[\alpha]_D = -26.36°$. Many other esters of cholesterol have been prepared, but the only ones that need be mentioned here are the oleate and palmitate, as they have been found in blood serum and in some pathological fluids.

Cholesteryl palmitate melts at 77° to 78°. *Cholesteryl oleate* is easily soluble in ether, chloroform, benzene, and hot acetone, but in alcohol is more difficultly soluble than cholesterol. It crystallises in needles, melts at 41°, and has a sp. gr. rotatory power $[\alpha]_D = -18.48°$.

It is insoluble in water, but is said to possess the peculiar property of taking up considerable quantities of water, forming a perfectly homogeneous salve-like, somewhat foamy mass, not unlike lanoline. It gives the cholesteryl colour indications (see later) in a modified manner.

The cholesteryl esters can be easily saponified by boiling with an alcoholic solution of potassium hydroxide, or, in the cold, by the action of sodium ethoxide—on the ethereal solutions.

Digitonin-cholesteride, $C_{27}H_{46}O.C_{55}H_{94}O_{28}$, is prepared, according to Windaus (*Ber.*, 1909, **42,** 240), by mixing a hot solution of 1 gm. digitonin in 100 c.c. 90% alcohol with a solution of 0.4 gm. cholesterol in 60 c.c. of 95% alcohol. The substance is precipitated in the crystalline form and, after standing for 1 hour, is filtered, washed with alcohol and dried at 110°. It is easily soluble in pyridine, but insoluble in cold water, acetone, ether, ethyl acetate and benzene. 100 c.c. methyl alcohol dissolves at 18° about 0.47 gm.; 100 c.c. 95% ethyl alcohol at 18° only 0.014 gm., and at 78° about 0.16 gm.; 50% boiling alcohol, 0.03 gm. The dry substance is very hygroscopic and gives in a typical manner the Burchardt-Liebermann test for cholesterol. It has no definite m. p., but decomposes gradually at 240°.

Phytosterol, coprosterol, stigmasterol and many alcohols of other series form similar compounds, but *the esters of cholesterol do not interact with digitonin.*

Oxidation.—The carbon skeleton of cholesterol is extremely stable, and though the substance is readily attacked by oxidising agents, the products are usually neutral or acid substances of the same carbon content. Oxidising agents usually attack the double linkage, or both the double link and the carbinol group; but Diels and Abderhalden (*Ber.*, 1904, **37**, 3092) found that when cholesterol is heated with powdered copper oxide to 280 to 300° the CH(O.H.) group is oxidised to CO, the ketone cholestenone being formed.

Cholestenone, $C_{27}H_{44}O$, is, however, more readily prepared by a method devised by Windaus (*Ber.*, 1906, **39**, 518). Cholesterol dibromide is oxidised either by chromic acid in glacial acetic acid solution at 70° or by means of an acid solution of potassium permanganate in the cold. The cholestenone dibromide thus formed is reduced by means of zinc dust and acetic acid, and the cholestenone obtained in a yield of 60%. Cholestenone melts at 81 to 82°, and forms a hydrazone, which crystallises in needles, m. p. 152°; a semicarbazone, m. p. 234°, and an oxime, m. p. 150°.

Detection of Cholesterol.—When moderately pure, cholesterol is easily recognised by its characteristic crystalline form. The substance to be tested should be boiled with 90% alcohol, the solution filtered hot and allowed to cool slowly. Either immediately on cooling, or after previous concentration, the cholesterol will be deposited in crystals, which, viewed under a moderate power appear as thin, very transparent, rhombic plates, the angles of which are well defined and constantly measure 79° 30′, and 100° 30′.

The most valuable tests are, however, the formation of the acetate, benzoate, dibromide and digitonin compound by the methods already described and the examination of their properties. The esters may be prepared with care from quantities of cholesterol as small as 0.05 grm. and the digitonin-cholesteride from quantities much smaller than this. These derivatives sometimes form a convenient means of separating cholesterol from other substances. By means of the digitonin compound cholesterol may be distinguished from its esters.

Cholesterol gives a number of well-marked colour indications which are sometimes useful and of which the following are the chief:

Schiff's Test.—Cholesterol is cautiously heated with a drop of concentrated nitric acid, and the pale yellow product treated with ammonia before it has completely cooled. A deep yellowish-red colour is developed which is not essentially altered by fixed alkalies. The indication, however, is not specific, as it is given by turpentine and other substances.

Moleschott's Test.—If a crystal is warmed on a microscope slide with a mixture of 5 volumes of concentrated sulphuric acid and 1 volume of water, cholesterol acquires a fine carmine-red; with 4 volumes of acid and 1 of water, it becomes blue without warming; with 3 acid to 1 water, violet, and 2 acid to 1 water, pale lilac.

Hydrochloric Acid Test.—When cholesterol is evaporated with strong hydrochloric and mixed with 1/3 of its volume of a solution of ferric chloride, the residue is coloured a fine red-violet, changing to blue-violet. Gold and platinum chlorides behave similarly to ferric chloride.

Salkowski's Test.—A few mg. of cholesterol are dissolved in about 2 c.c. of chloroform and then shaken with an equal bulk of strong sulphuric acid. The chloroform quickly becomes blood-red and then cherry-red or purple, a colour which it retains for several days. A few drops of this solution poured into a basin become blue, green, and then yellow, owing to the absorption of water. The original colour may be again restored on adding some sulphuric acid. The sulphuric acid which separates from the chloroform presents a distinct fluorescence.

Burchardt-Liebermann Test.—A few mg. of cholesterol are dissolved in 2 c.c. of chloroform, 20 drops acetic anhydride are added, and a single drop of concentrated sulphuric acid. A violet pink colour is developed. This test is very delicate, but the indication is shared by resin acids and other substances. More or less similar colour indications are given by many derivatives and isomers of cholesterol, and by other allied substances.

Isocholesterol.—This body is isomeric with ordinary cholesterol and occurs with it in wool-fat. It has not, however, so far as the writer is aware, been found in any of the organs or tissues of the animal body.

To separate cholesterol and isocholesterol, the mixture should be heated for 30 hours in a sealed tube to 200°, with 4 times its weight of benzoic acid or benzoic anhydride. The product is then repeatedly boiled with rectified spirit, when excess of benzoic acid dissolves and the cholesteryl and incholesteryl benzoates remain. By crystallising from ether, the former is obtained in shining rectangular plates and the latter as a light crystalline powder which may be separated by decantation and elutriation.

Isocholesterol benzoate after recrystallisation from ether is obtained in the form of minute needles melting at 190 to 191°.

Isocholesterol is obtained by saponifying the benzoate with alcoholic solution of potassium hydroxide. It separates from absolute alcohol in flocks when the solution is dilute, but a concentrated solution solidifies as a transparent jelly. From ether it is deposited in needles. It melts at 137° to 138°, and has a specific rotatory power $[\alpha]_D = +60°$, which is independent of the concentration of the solution. Isocholesterol gives the Schiff's test (page 483), but shows no colour changes with sulphuric acid and chloroform or with ferric chloride and a mineral acid. With the Burchardt-Liebermann test (page 483) a yellow and afterward a yellowish-red colouration appears, with, at the same time, a green fluorescence. Isocholesteryl acetate is obtained by digesting the alcohol with acetyl chloride until the evolution of hydrogen chloride ceases, and then heating to 100° in a sealed tube. On removing the excess of acetyl chloride by evaporation, isocholesteryl acetate is obtained as an amorphous substance. It is readily soluble in alcohol, and melts below 100°.

Vegetable Cholesterols.—Cholesterol is represented in the vegetable kingdom by the isomeric substance, phytosterol, which appears to be equally widely distributed. After the discovery of this substance by Hesse in calabar beans and peas in 1878 (*Ann.*, 1878, **192**, 178), many different plants were examined by various observers; and a large number of substances, all very similar in properties and melting between 130° and 137°, were described. A list is given in table I.

TABLE I.

Name of chemist	Source of the phytosterol	Name of phytosterol	M. p.	Formula assigned	M. p. of acetate	M. p. of benzoate	References	Remarks
(1) Beneke	Seed peas, green plants, seeds, and blossom parts.		136°–137°				*Ann.*, 1862, **122**, 249.	Considered by the writers to be cholesterol.
(2) Ritthausen	Wheat gluten						Jahresb. d. Fortsch. d. Chem., 1863, 544.	
(3) Lindenmeyer	Peas, various oils						*J. prakt. Chem.*, 1863, **90**, 328.	
(4) Hoppe-Seyler	Maize, rape oil and almond oil.						*Med. Chem. Untersuchung*, 1866.	
(5) Tschirch	Grass						Burian, *Monatsh.*, 1897, **18**, 570.	
(6) Wallerstein	Barley						Cohen, "Ueber Lupeol," Diss., Utrecht, 1906.	
(7) Hesse	Calabar beans	Phytosterol	132°–133°	$C_{26}H_{44}O + H_2O$(?)	120°		*Ann.*, 1878, **192**, 175.	
(8) König	Meadow hay	Phytosterol	134°				Cohen's Diss. über Lupeol Tables, 1906.	
(9) Reinke and Rodewald.	Æthalium septicum	Paracholesterol	134°	$C_{26}H_{44}O$(?)		127°–128°	*Ann.*, 1881, **207**, 229.	
(10) Lippmann	(Beet juice (Rübensaft).	Phytosterol					*Ber.*, 1887, **20**, 3201.	
(11) Arnaud	Beets (Rüben)	Carotol	136.5°	$C_{26}H_{44}O$(?)			*Ber.*, 1886, **19**, 105.	Considered identical with Hesse's phytosterol.
(12) Husemann	Daucus carota	Hydrocarotol	126.5°				*Ann.*, 1861, **117**, 200.	
(13) Reinitza	Roots of carrots	Hydrocarotol	137.4°		127.6°	144°	*Monats. Chem.*, 1887, **7**, 597.	
(14) Schulze and Barbieri.	Triticum vulgare, folium perenni.	Phytosterol	136°	$C_{26}H_{44}O + H_2O$(?)			*J. prakt. Chem.*, 1882, **25**, 159.	
(15) Paschkis	Colchicum seeds	Phytosterol	133°	$C_{26}H_{44}O + H_2O$(?)			*Zeit. phys. Chem.*, 1884, **8**, 356.	
(16) Likiernik	Pisum sativum (Lens esculenta).	Phytosterol	135°		120°	145°	*Zeit. phys. Chem.*, 1891, **15**, 430.	
(17) Salkowski	Adulterated codliver oil.	Phytosterol	132°–134°				*Zeit. anal. Chem.*, 1887, **26**, 557.	
(18) Bukowsky	Oil from lycopodium seeds.	Phytosterol					*Chem. Centralbl.*, 1889, **60**, 156.	About 0.3%.
(19) Hesse	Aristolochia argentina	Phytosterol		$C_{26}H_{43}OH$(?)			*Archiv. d. Pharm.*, 1895, **233**, 684.	As palmitic ester.
(20) Dunstan and Chaston.	Roots of scopolia carniola.	Phytosterol	137.5°	$C_{26}H_{44}O$(?)		145.5°	Vide Cohen., Diss. über Lupeol.	

TABLE I.—Continued.

Name of chemist	Source of the phytosterol	Name of phytosterol	M. p.	Formula assigned	M. p. of acetate	M. p. of benzoate	References	Remarks
(21) Jacobson	Broad beans	Phytosterol	131.5°–132.5°	$C_{26}H_{44}O+H_2O$	126°	145°–145.5°	*Zeit. physiol. Chem.*, 1888, **13**, 32.	Reckoned as cholesterol.
(22) Jacobson	Sweet peas	Phytosterol	134°–135°		119°–620°	147°		
(23) Jacobson	Peas	Phytosterol	132°–133°		117°–118°	145°–146°		
(24) Jacobson	Lupins	Phytosterol	136.5°		124°–125°	144°–145°		
(25) Bömer	Cottonseed and fatty oils.	Phytosterol	136°–137°	$C_{27}H_{46}O$	123°–126°	142°–143°	*Zeit. Nahr. Genuss.*, 1899, **2**, 705. *Zeit. Nahr. Genuss.*, 1901, **4**, 865.	Phytosterol were also found in various other oils, but not sufficiently investigated.
(26) Bömer	Sesame oil and linseed oil.	Phytosterol	137°–137.5°		128°–129°	145°–146°		
(27) Bömer	Rape oil	Phytosterol	139°–140°		134°–636°			
(28) Villa Vecchia and Fabris.	Sesame oil	Phytosterol	137.5°	$C_{25}H_{44}O+H_2O$(?)	...	...	*Chem. Centralbl.*, 1897, Bd. **2**, 172.	
(29) Schweissinger	Rape oil	Phytosterol	133°	...	...	...	*Chem. Centralbl.*, 1891, **2**, 229.	
(30) Burian	Wheat germ	Sitosterol	137.5°	$C_{27}H_{44}O+H_2O$	127°	145°–148.5°	*Monatsheft. Chem.*, 1897, **18**, 553.	(Pure phytosterol.)
(31) Burian	Mother liquors of above.	Parasitosterol	127.5°		115°–120°		*Monatsheft Chem.*, 1897, **18**, 566.	
(32) Ritter	Wheat germ	Sitosterol	136.5°		...	145.5°	*Zeit. phys. Chem.*, 1902, **34**, 461.	Various other esters.
(33) Gérard	Brewer's yeast	Plant cholesterol.	135°–136°	...	...	Could not purify.	*J. pharm. Chim.*, [6], 1895, **1**, 601–608.	
(34) G. Sani	Olive oil	Phytosterol	134°	...	...	149°	*Chem. Centralbl.*, 1903, **1**, 93.	
(35) Rümpler	Beet root	Betasterol	117°	$C_{26}H_{44}O$	...	...	*Ber.*, 1903, **36**, 975–976.	
(36) Gill and Tafts	Maize oil	Phytosterol	137.5–138°°	...	...	...	*J. Amer. Chem. Soc.*, 1903, **25**, 251.	
(37) Power and Tutin.	Eriodictyon californicum.	Phytosterol	136°–137°	...	...	...	*Pharm. Rev.*, 1906, **24**, 300–304.	Very small and identical with sitosterol.
(38) Windaus and Hauth.	Calabar bean	Phytosterol	137°	...	127°	146°	*Ber.*, 1907, **40**, 3681–3686.	
(39) Tarbowa and Hardy.	Roots of Echinophora spinosa.	Phytosterol	148°	...	124°–125°	145°	*Bull. Sci. Pharm.*, 1907, **14**, 387–392.	
(40) Windaus and Welsch.	Rape oil	Phytosterol	142°	$C_{27}H_{26}O$	134°	142°	*Ber.*, 1909, **42**, 612.	Authors not quite certain of purity of specimen.
(41) Henze	Suberites domuncula	Spongosterol	123°	$C_{27}H_{48}O$	124°	128°	*Zeit. physiol. Chem.*, 1904, **41**, 109.	
(42) Dorée	Cliona ciliata	Clionasterol	137°	$C_{27}HO_{46}$	133°	143°	*Biochem. J.*, 1909, **4**, 74	

It seems probable from the recent work of Windaus and Hauth (page 493) that these consist of one and the same substance in different degrees of purity. This substance is identical with the phytosterol of wheat germ, which was first isolated and carefully examined by Burian (*Monatsh.*, 1897, **18**, 572). Besides these low melting phytosterols a number of products of higher m. p. have been isolated. Of these we may mention caulosterol, isolated by Schulze and Barbieri (*J. pr. Chem.*, 1882, **25**, 160) from the cotyledons and hypocotyledonous parts of lupins, which melted at 158–159°; and stigmasterol, m. p. 170° (see later, page 493). According to Gérard (*Compt. rend.*, 1892, **114**, 1544) the phytosterols of cryptogams quite generally appear to differ from those of phanerogams by having a higher m. p. The best known representative of the first group is the ergosterol of Tanret (*Compt. rend.*, 1908, **147**, 75), isolated from ergot, which melts at 165° and possesses an unusually high rotation. This substance, according to Tanret, undergoes a slow decomposition under the influence of light.

Besides the above-mentioned true phytosterols, which are isomeric with animal cholesterol, a great number of phytosterol-like substances have been found, which differ in their composition from cholesterol. Thoms (*Arch. Pharm.*, 1897, 235, 39) has proposed to include these substances under the general heading phytosterols—as they are unsaturated alcohols of high molecular weight, give the colour reactions of the cholesterol group, and owe their origin to physiological processes similar to those which produce phytosterol. It is, however, difficult to know where to draw the line. A list is given in Table II.

Phytosterol (sitosterol of Burian), $C_{27}H_{46}O$, is easily soluble in ether, chloroform, benzene, and carbon disulphide, sparingly soluble in cold alcohol, but readily in hot. Like cholesterol, it crystallises from 90% alcohol with $1H_2O$. It crystallises from alcohol in fascicular well-formed fairly broad crystals, and when the crystallisation is slow the crystals assume the form of 6-sided tablets. It melts at 137°, and in ether solution has a specific rotatory power $(\alpha)_D = -26.71°$.

Phytosteryl acetate, $C_{27}H_{45}.C_2H_3O_2$, is prepared in a similar manner to cholesteryl acetate. It melts at 127°.

Phytosteryl propionate, $C_{27}H_{45}C_3H_5O_2$, melts at 108°.

Phytosteryl benzoate is prepared by heating phytosterol with benzoic anhydride or benzoyl chloride, but is not readily obtained by the action

TABLE II.

Substances of high m. p., analogous to Phytosterol

Author	Material used	Name of substance and formula given	M. p.	M. p. of acetate	M. p. of benzoate	References	Remarks
Schulze and Barbieri.	Lupins	Caulosterol, $C_{26}H_{44}O+H_2O$	158°–159°	....	145°	*J. pr. Chem.*, [2], 1882, **25**, 159.	Partly from roots and partly from parts above ground.
Likiernik	French beans (Phaseolus vulgare).	Paraphytosterol....	149°–150°	....	142°–143°	*Zeit. physiol. Chem.*, 1891, **15**, 427, and *Ber.*, 1891, **24**, 187.	
Marino-Zuco	Chrysanthemum flowers	$C_{28}H_{48}O$(?)	183°	223°	246°	*Gazzetta*, 1889, **19**, 209.	
Tanret	Ergot	Ergosterol	154°	169°–175°	154°	*Compt. rend.*, 1889, **108**, 98.	
Likiernik	Peelings of lupin seeds .	Lupeol, $C_{31}H_{49}OH$(?)	211°	214°	265°–266°	*Zeit. physiol. Chem.*, 1891, **15**, 415.	
Klobb	Chamomile (Anthemis nobilis).	Anthesterol, $C_{28}H_{48}O$	222°–223°	....	284°–286°	*Bull. Soc. Chim.*, 1902, **27**, 1229.	
Vesterberg	Gum elemi..........	α-amyrol, $C_{30}H_{50}O$	185°	220°–221°	192°	*Ber.*, 1887, **20**, 1242.	
Hesse	Coca beans	β-amyrin, $C_{30}H_{50}O$(?)	195°	235°	230°	*Ann.*, 1892, **271**, 214.	
Marck	Milky juice of Asclepias syriaci.	β-amyrin, $C_{28}H_{46}O$(?)	181°–182°	201°–202°	195°–196°	*J. pr. Chem.*, 1903, **68**, 449.	
Bauer	Appopunax	Chironol, $C_{28}H_{48}O$ ...	176°	196°	188°	*Archiv. Pharm.*, 1895, **233**, 233.	
Bickern	Seeds of Casimiroa edulis.	Casimirol, $C_{27}H_{48}O_2$..	207°	....	....	*Arch. Pharm.*, 1903, **241**, 173.	
Sack and Tollius....	Brask (Borneo) from sap of Alstonin costulata.	Alstol, $C_{24}H_{38}O$(?) ..	158°	200°	254°	*Ber.*, 1904, **37**, 4110.	
Sack and Tollius....	Bark of Soucheria griffithriana.	Lupeol, $C_{26}H_{42}O$.....	213°	....	262°	*Ber.*, 1904, **37**, 4110......	Identical with lupeol of Likiernik.
Ottolenghi	Ergot	Ergosterol, $C_{24}H_{40}O+H_2O$(?).	....	165°	....	*Centralbl.*, 1906, **1**, 541.	
Thoms	Ononis roots	Onocerol, $C_{26}H_{42}(OH)_2$ (?)	232°	224°	178°–190°	*Ber.*, 1896, **29**, 2985.	
Klobb	Arnica montana	Arnidiol, $C_{28}H_{44}(OH)_2$ (?)	249°–250°	....	223°–228°	*Bull. Soc. Chim.*, 1905, **33**, 1075.	
Hinsberg and Roos..	Yeast fat	Cholesterol of yeast..	159°	....	....	*Zeit. physiol. Chem.*, 1903, **38**, 12.	
Windaus and Hauth.	Calabar beans	Stigmasterol, $C_{30}H_{48}O$	170°	141°	160°	*Ber.*, 1907, **40**, 3681.	Along with phytosterol.
Power and Tutin....	Leaves of Olea europæa.	Oleasterol, $C_{20}H_{33}OH$	174°	....	....	*Trans.*, 1908, 891.	
Power and Tutin....	Leaves of Olea europæa.	Olestranol, $C_{25}H_{42}O_2$.	217°–218°	Syrup.	Syrup.		Colour reactions showed it to be different from casimirol.
Power and Tutin....	Leaves of Olea europæa.	Homo-olestranol, $C_{27}H_{46}O_2$.	210°	....	....		
Windaus and Welsch,	Rape oil............	Brani casterol	148°	157°–158°	167°	*Ber.*, 1909, **42**, 612.	

of benzoyl chloride on a pyridine solution of the alcohol. It crystallizes in oblong rectangular leaves and melts to a clear liquid at 146°. When the melted substance cools, a play of colours at that point of solidification is observed—yellowish-green, blue, and faint red. An account of the esters formed by phytosterol with the higher fatty acids will be found in a paper by Ritter (*Zeit. physiol. Chem.*, 1902, **34**, 430). Gill and Tufts (*J. Amer. Chem. Soc.*, 1903, **25**, 251, 498), and also Schulze and Winterstein (*Zeit. physiol. Chem.*, 1905, **43**, 316) found that phytosterol undergoes a change on standing in the air, which causes a lowering of m. p. According to Polenske and also C. Virchow (*Chem. Centr.*, 1897, **II**, 395), if animals are fed with phytosterol or foods containing phytosterol, no phytosterol is found in their fat, nor in the writer's experience, in other tissues or organs.

Isolation and Estimation of Cholesterol and Phytosterol. Examination of Ether Residues.—For the separation of cholesterol, phytosterol, and similar substance from animal or vegetable matter, the latter must be reduced to a dry friable substance, easily capable of extraction by ether or other solvents. Some substances may be simply dried in the oven and coarsely powdered; others, such as organs and flesh of animals, must be shredded and minced in a machine and then thoroughly ground in a mortar with sand before drying. Liquids, such as blood, containing much coagulable proteid are conveniently mixed with sand and plaster of Paris in such quantity that the mass sets solid. The solid is then powdered. This method is also very convenient in the case of brain, eggs, etc. The dried substance should be exhausted with ether, as described on page 490.

The ether extracts consist of fats, phosphorised fats, such as the lecithins, alcohols, such as cholesterol, phytosterol, etc., and indeterminate unsaponifiable matter. It has been stated by Dormeyer (*Pflüger's Archiv.*, 1906, **61**, 341–343) that the fat cannot be quantitatively extracted from animal organs in a Soxhlet's apparatus with ether, and he recommends that the tissue be subjected to artificial gastric digestion before extraction. In the writer's experience, however, if the material is properly prepared for extraction by the above methods and the extraction be sufficiently prolonged, this difficulty can be overcome.

The ether extract, after distilling off the ether, is saponified by alcoholic solution of potassium hydroxide, the alcohol evaporated, and the unsaponifiable matter extracted from the aqueous solution of the resultant soaps by agitation with ether in the manner described on page 490. When oils or fatty matters are to be examined, they may be at once saponified by alcoholic potassium hydroxide. The chief practical difficulty met with in this procedure is the formation of emulsions of soap solution and ether which sometimes persist for long periods. Further, large quantities of ether are required for complete separation of cholesterol from the soap solution. Many methods have been proposed by various writers to overcome these and other difficulties and to obtain the cholesterols in a state sufficiently pure for weighing. A detailed critical examination of these methods has been made by Ritter (*Zeit. physiol. Chem.*, 1902, **34**, 430), for an account of which the original memoir must be consulted.

Ritter recommends the following method:

50 grm. of fat are heated on the water-bath in a large porcelain basin with 100 c.c. of alcohol and a solution of 8 grm. of sodium in 150 c.c. of 99% alcohol. When the alcohol has volatilized, 75 grm. of sodium chloride are added and then so much water that the greater part of the mass dissolves. This liquid is evaporated to dryness, first over the naked flame, then on the water-bath, and finally in the drying oven at 80°. The residue is finely powdered, placed in a paper cartridge, and extracted with ether in a Soxhlet extractor during 9 hours. To remove traces of soap and glycerol the ether is distilled off, the residue dissolved in as little alcohol as possible, and reprecipitated by water. The "cholesterol" is collected on a filter and dried at 60°. The bulk of it is transferred to a weighed flask, and the last adhering particles are rinsed off with ether. The ether is evaporated and the residue dried at 100 to 120°. The method gives satisfactory results, provided no other unsaponifiable matter besides cholesterol or allied substances is present.

The writer, however, prefers to use the method of saponification by means of sodium ethoxide proposed by A. Kossel and K. Obermüller (*Zeit. physiol. Chem.*, 1890, 14, 599). To the unevaporated ether extract, or the dilute solution of the fat in ether, an excess of sodium ethoxide in concentrated alcoholic solution is added, when the fat is saponified in the cold and the soap is precipitated—often in an easily filterable form. After standing several hours the soap is filtered off and thoroughly washed with a large excess of ether. The filtrate is then *repeatedly* washed in a separating funnel, first with water and then with a dilute solution of potassium or sodium hydroxide to get rid of alcohol, glycerol, excess of alkali, and small quantities of soap that dissolve in the ether. The ethereal solution is then dried with calcium chloride, filtered, and the ether distilled off. If the soap is large in bulk, or if it happens to be difficult to filter, it is advisable to mix the soap (filter-paper included) with an equal weight of salt, partially dissolve and evaporate to dryness, as in Ritter's method. The dry mass is powdered and re-extracted with ether. The ethereal extract may be added to the main filtrate from the soap. If the fat dealt with is liquid and rich in olein, the ethereal filtrate from the soap must be very thoroughly washed, as alkali oleates are more soluble in ether than other soaps. When no other unsaponifiable matter is present, the ether residue will consist of cholesterol and phytosterol and may be sufficiently pure to be weighed. Usually, however, this is not the case and further purification is necessary. The cholesterol in such a residue may be estimated by either of the methods of Lewkowitsch (*Ber.*, 1892, **25**, 65–66). The first method depends on the quantitative formation of an acetate of cholesterol when the latter is boiled with acetic anhydride; the acetate is washed with warm water until no longer acid, and its amount estimated by boiling with alcoholic potash of known strength and titrating back with standard acid.

The second method depends on the formation of a diiodide. The cholesterol is dissolved in chloroform (50 c.c.) mixed with v. Hübl's solution of iodine and mercuric chloride in alcohol (25 c.c.), and the excess of iodine determined by sodium thiosulphate. The calculated iodine absorption values for cholesterol and phytosterol are 68.3. Lewkowitsch actually obtained for cholesterol, 68.09 and 67.3.

In working with purely animal products the writer prefers to convert the cholesterol into the benzoate by the action of benzoyl chloride on the pyridine solution of the residue (see page 480) and weigh the recrystallised cholesteryl benzoate, in which case a correction may be made for the solubility in alcohol.

Pure cholesterol can easily be distinguished from phytosterol by the form and grouping of the crystals. If both substances are present, the mixture crystallises in one form only, the crystals either approximating to the form of phytosterol, or if cholesterol is present in the greater quantity, differing from the pure crystals of either body.

Separation of Phytosterol from Cholesterol.—The presence of phytosterol mixed with cholesterol may be detected by the examination of the acetate. Cholesteryl acetate melts at 113°; phytosteryl acetate, at 128°; both acetates form isomorphous mixtures and through the addition of phytosteryl acetate to cholesteryl acetate the m. p. of the latter is raised.

A good method of separating cholesterol and phytosterol has been given by Windaus (*Chem. Zeit.*, 1906, **30,** 1011) depending on the different solubilities of the dibromides in a mixture of ether and glacial acetic acid. The best way of treating any given mixture will be gathered from the following description taken from his paper:

1. A mixture of 4 grm. of cholesterol and 4 grm. of phytosterol was dissolved in 80 c.c. ether, and 80 c.c. of a solution of 5 grm. of bromine in 100 c.c. glacial acetic acid were added, and allowed to stand at 0° for 1 hour. The crystalline precipitate (A) which formed was filtered and washed with 4 c.c. glacial acetic acid and then with 4 c.c. of 50% acetic acid. The washings were added to the main filtrate when another precipitate (B) was obtained. A and B, after washing with water and drying, weighed, respectively, 3.7 and 1.4 grm. These precipitates were mixed and heated under a reflux condenser with 100 c.c. glacial acetic acid and 5 grm. of zinc dust for 2 hours; the excess of zinc was filtered off and the solution treated with a large quantity of water. The precipitate was boiled for two hours with 100 c.c. of 10% alcoholic potassium hydroxide, and the cholesterol thrown out of solution by the cautious addition of water. After recrystallization from alcohol, 2.7 grm. of cholesterol, melting at 146°, were recovered. The filtrate from B, which contained the phytosterol dibromide was also heated for 2 hours with zinc dust, and the product treated in the same way as cholesterol. The yield of phytosterol was 2.8 grm. It melted at 134 to 136° and its acetate at 126 to 127°.

2. In this experiment a mixture of 8 grm. of cholesterol with 0.8 grm. of phytosterol was taken. The precipitate (A) weighed 8.1 grm., (B) weighing 1.82 grm. The solution which contained the phytosterol-dibromide along with a little cholesterol-dibromide was treated as follows: zinc dust was added, the ether distilled off, and the remaining solution was boiled for 2 hours. The organic matter was thrown out of solution by the addition of water and taken up in ether. The ethereal solution was freed from acid by shaking with potassium hydroxide, evaporated, the residue acetylated by boiling with acetic anhydride and the acetate twice recrystallized from alcohol. It melted at 125 to 127° and weighed 0.31 grm.

3. In this experiment a mixture of 4 grm. phytosterol and 0.4

grm. cholesterol was taken and treated as before. On the addition of the solution of bromine in acetic acid no precipitate was formed, but a precipitate (A) settled out on the further addition of 11 c.c. of 50% acetic acid. This weighed 0.14 grm. and consisted of pure cholesterol dibromide. It was washed with 2.2 c.c. of glacial acetic and 11 c.c. of 50% acetic acid. On the addition of the wash liquor to the main solution a precipitate (B) was thrown down weighing 0.24 grm. This was not quite pure. From the filtrate about 3 grm. of phytosteryl acetate was prepared.

The methods of separation of phytosterol from allied substances of higher m. p. and from the aliphatic alcohols have not as yet been thoroughly worked out. Windaus and Hauth have, however, recently made an important advance in this direction by their separation of the phytosterol obtained by Hesse from calabar beans into its constituents. (Hauth, Inaugural Dissertation, Freiburg, 1907). Hesse's phytosterol melted at 132 to 133° and under the microscope appeared to be perfectly homogeneous. This substance was converted into the acetate. 20 grm. of this acetate was dissolved in 300 c.c. of ether and 250 c.c. of a 5% solution of bromine in glacial acetic acid added and the whole allowed to stand. A copious deposit of small hard crystals separated which was washed successively with glacial acetic, dilute acetic acid, and water. After recrystallization from alcohol the material melted at 211 to 212°, and had the composition $C_{30}H_{50}O_2Br_4$. On reduction with zinc dust and glacial acetic acid an acetate was obtained which, after recrystallization from alcohol, melted at 141°. This acetate on saponification with alcoholic potassium hydroxide gave an alcohol of the formula $C_{30}H_{48}O$, which was named *stigmasterol*, melted at 170°, and was sparingly soluble in most solvents, with the exception of ether and chloroform. In ether solution it had a specific rotatory power $(\alpha)_D = -44.67°$. The crystals were very similar to those of phytosterol and showed the typical colour reactions of the cholesterol group.

The *propionate* melted at 122°, and the *benzoate* at 160°.

The filtrate from the tetrabromide contained phytosterol acetate dibromide. This after reduction and saponification yielded pure phytosterol. The percentage of stigmasterol in the original material was 20%.

The two alcohols, stigmasterol and phytosterol, are isomorphous and scarcely differ crystallographically.

From this work it would seem probable that the so-called isomers of true phytosterol which differ from it slightly in m. p. consist of phytosterol mixed with stigmasterol or similar substances. In the one other case examined—the phytosterol of rape oil—this inference proved correct (Windaus and Welsch, *Ber.*, 1909, **42,** 612). When the distribution of stigmasterol and like substances in the vegetable world has been more carefully studied, their presence or absence may form a useful test for the adulteration of one vegetable oil with another.

For the approximate separation of the constituents of a complex ether residue, such as that yielded by "recovered grease" or the crude oleic acid obtained by the distillation of such products, Schulze (*J. prakt. Chem.*, 1873, N. F., **7,** 163) has given the following method: The ether residue is boiled for an hour or two with an equal weight of acetic anhydride. The hydrocarbons, such as petroleum, vaseline, cerasin, and paraffin, are not dissolved, but form an oily layer on the surface of the acetic anhydride, and may be separated while the liquid is still hot. The acetic anhydride solution is boiled several times with water to decompose the excess of anhydride. The residue consists of acetates of the solid alcohols, and if boiled with sufficient alcohol will dissolve entirely, but on cooling the solution the cholesteryl acetate will crystallize out almost completely. The acetates of the alcohol radicals form sperm oil and the waxes remain in solution, and are precipitated as an oily layer by pouring the liquid into hot water. For the identification of wax alcohols, see article on Waxes.

WOOL-FAT. WOOL-GREASE. SUINT. DEGRAS (U. S.)

By AUGUSTUS H. GILL, Ph. D.

Sheep's wool contains a large amount of fatty matter of very peculiar character. It is excreted by all parts of the skin, but is found most abundantly about the breast and shoulders. The crude "yolk," as it is called, is largely soluble in water, and hence is removed by washing the wool, but the wool-fat or suint proper remains, and can be extracted by carbon disulphide, petroleum spirit, ether, or other suitable solvent.

Thus obtained, wool-fat is a yellow or brownish grease, having a peculiar disagreeable smell. It melts between 39 and 43° and has a sp. gr. of about 0.973 at 15°. It possesses the remarkable property of forming a good emulsion with water, which when kept at the ordinary temperature exhibits no tendency to separate. Complete saponification of wool-fat cannot be effected by boiling with alcoholic potassium hydroxide except under pressure. It can, however, be quickly saponified by the method of Kossel-Obermüller, using sodium ethylate prepared by dissolving 5 grm. of sodium in 110 c.c. absolute alcohol.

Wool-fat has a complex composition; the exact nature of which is still unknown. Cholesterol and isocholesterol are present and potassium salts of several fatty acids, some of them volatile. Contrary to the usually accepted statements, Lewkowitsch (*J. Soc. Chem. Ind.*, 1892, **11**, 136; 1896, **15**, 14) has found that wool-fat is not a mixture of cholesteryl and isocholesteryl stearates, palmitates, and oleates, as is shown by the low iodine absorption of both the fatty acids and the alcohols. The former were found to consist of hydroxy-acids, easily giving off the elements of water at temperatures little above 100° with formation of inner anhydrides or lactones. Oleic acid, if present, is in small amount. Besides cholesterol, a considerable proportion of lower *saturated* alcohols is present. No glyceryl esters have been found in wool-fat.

Darmstädter and Lifschütz (*Ber.*, 1897, **29**, 2890), have reported the isolation of the following bodies: *Lanoceric acid*, $C_{30}H_{60}O_4$, insoluble in water, but easily soluble in hot alcohol, from which it crystallises, on cooling, in plates of m. p. 103 to 105°; *lanopalmitic acid*, melting at 87 to 88° and solidifying at 83 to 85° to a lustrous crystalline mass, and having the property of readily forming an emulsion with water; also *carnaübic* and *myristic acids*, an oily acid apparently *oleic*, and a volatile acid, possibly *caproic*. Among the alcohols, separated by absolute alcohol into several fractions, ceryl, carnaübyl alcohol (saturated), and cholesterol were identified. The investigations of G. de Sanctis (*Chem. Zeit.*, 1895, **19**, 651) point to the presence also of *palmitic* and *cerotic* acids.

The results of Lewkowitsch's inquiries into the nature of wool-fat (*J. Soc. Chem. Ind.*, 1892, **11**, 135; 1896, **15**, 14) have led him to conclude that it is a true wax in the strict sense of this generic term. Natural wool-fat resembles beeswax, its closest relative, in that it contains a considerable proportion of free acid and a small amount of free alcohols, besides true waxes, and the term wool-wax should therefore be substituted for wool-fat; but considering the fact that the commercial wool-fat is, as a rule, contaminated with fatty acids derived from the soap used in scouring the wool, it is more convenient to retain the term wool-fat for the commercial product. He proposes, therefore, that the name wool-wax be given to the neutral portion of the wool-fat. This consists of a mixture of true wax and alcohols, the former predominating considerably. The name wool-wax appears all the more desirable, as this neutral portion is now obtained in large quantities, both in the anhydrous and hydrated state, and confusion with the crude wool-fat is thereby avoided.

The following are the results of examinations made by Lewkowitsch, as well as some estimations made in Allen's laboratory by W. Chattaway:

WOOL-WAX (ESTERS AND FREE ALCOHOLS).

	Lewkowitsch.	Chattaway.
Sp. gr. at 98.5° (water at 15.5° = 1)	....	.9017[2]
M.p.	31°–35°[1] 39°–41°	....
Solidifying-point	30°–30.2°[1]	....
Percentage of potassium hydroxide for saponification	10.24[1]	9.83[2]
Saponification-equivalent	....	901.7[2]
Iodine absorption	25.8–28.9[1] 17.1–17.6[2]	....
Fatty acids, %	59.8	....
Alcohols	43.6 51.84[2]	....

	Mixed fatty acids	Mixed alcohols
Solidifying-point	40°	28°[1]
M. p.	41.8°	33.5°
Mean molecular weight	327.5	239
Iodine absorption	17.5	36[1] 26.4[2]

NEUTRAL ESTERS.

Potassium hydroxide for saponification, %	9.69
Fatty acids, %	56.66
Alcohols, %	47.55

When extracted by means of solvents, wool-fat contains simply the constituents (fatty acids, neutral esters, alcohols, and potassium salts of lower fatty acids) natural to the wool. The following table represents the results of examination of wool-fat extracted by ether (Herbig, *J. Soc. Chem. Ind.*, 1894, **13**, 1069):

Source	Potassium salts in ash, calculated to potassium oleate	Free acid potassium hydroxide required	Percentage of potassium hydroxide for saponification on heating for one hour		Unsaponifiable matter (alcohols)
			Open flask	Closed flask	
New Zealand wool	4.9	14.3	10.60–10.82	11.05–11.07	43.66–43.94
Australian wool	4.24	15.5	10.25–10.35	11.27–11.32	....
South American wool	9.25	13.2	8.82–9.14	9.86–9.89	43.15–43.65
Russian wool	24.4	13.9	7.77–7.83	9.41–9.58	38.72–39.10

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[1] From raw wool-fat. [2] Prepared from "lanolin."

Wool-fat prepared by acidifying the suds obtained in the wool-scouring process is of irregular composition. Potassium salts of the lower fatty acids are present in but small quantity, since these are removed in the first stage of the process, which consists in steeping the wool in luke-warm water. In addition to the compounds mentioned above as naturally present in the wool, it may contain unsaponified fat and mineral oil which had been added to lubricate the wool and fatty acids derived from the soap used in scouring. The product obtained in this way is called *recovered grease*, *wool-grease*, *brown grease*, and *Yorkshire grease*. In the United States it is incorrectly called "dégras." (For a description of true "dégras" see under that head.)

The analysis of wool-fat requires a departure from the usual methods. The potassium and other mineral constituents can be estimated in the ash obtained on ignition. On saponifying the fat and extracting the soap in the manner described below, the *alcohols*, including cholesterol, are dissolved, recovered by evaporation of the solvent, and examined as described under "cholesterol." By treating the soap with acid, the *higher fatty acids* will be obtained, while the *lower fatty acids* can be estimated by distillation in the usual way. Foreign saponifiable fats will be indicated by the presence of glycerol in the aqueous liquid separated from the fatty acids, and their amount will be roughly indicated by multiplying the glycerol found by 10.

Free Fatty Acids.—These are measured by treating a weighed portion of the fat with alcohol, and titrating with standard potassium hydroxide in the usual manner; the amount may be calculated from the mean molecular weight. Lewkowitsch (*J. Soc. Chem. Ind.*, 1892, **11**, 136) separates the free fatty acids for the estimation of the molecular weight as follows: The amount of alkali required for neutralisation is first ascertained by titrating a small weighed quantity of the fat. A larger weighed quantity is then dissolved in alcohol and nearly neutralised with the greater part of the alkali required, and the remainder is added cautiously until the solution becomes pink to phenolphthaleïn. The mixture of neutral fat and unsaponifiable matter, which rises to the surface, is dissolved in ether and separated from the soap solution, which is then repeatedly shaken out with ether. The ethereal extracts are united and washed repeatedly with water to remove all traces of soap. This stage of the process is very tedious on account of the emulsification of the two liquids. There is also formed an intermediate layer, consisting of soap of a higher fatty acid, which is not soluble in water, but dissolves readily in boiling alkaline solution of soap of the other acids. It is separated by filtration. The free fatty acids are thus obtained in 2 parts, those of the dissolved soaps and those of the difficultly soluble soaps. The ether dissolved in the soap solution is distilled off and the fatty acids set free by acidulating with hydrochloric acid. The solid soap on the filter is treated with boiling water and hydrochloric acid for the same purpose.

Cochenhausen (*Ding. Poly. J.*, 1894, **292**, 91, 112) modifies the above process as follows: The neutralised wool-fat is shaken with 30% alcohol and the soap solution boiled down to dryness, dissolved in 50% alcohol, and exhausted with petroleum spirit. In this process also insoluble soaps of higher fatty acids separate between the two layers as flocculent matter and must be filtered off.

As noted above, wool-fat contains hydroxylated fatty acids, which, on heating to a temperature of 100° and over, lose the elements of water and form inner anhydrides or lactones. These are not completely hydrolysed by aqueous solution of potassium hydroxide, which, if used for ascertaining the molecular weight on a sample which has been heated to dry it, would furnish results in excess of the truth. Error from this source is avoided by boiling the acids with standard alcoholic potassium hydroxide and titrating back the excess of alkali. In this way any anhydride which may be present is effectually hydrolysed.

Saponification-equivalent.—As already noted, wool-fat is not completely saponified by simple boiling with alcoholic potassium hydroxide. Lewkowitsch (*J. Soc. Chem. Ind.*, 1892, **11**, 137) found that complete saponification could be effected by the use of 2N alkali under pressure. The fat and alkali should be contained in a copper flask tightly closed, placed in boiling water, and allowed to remain for from 1 to 2 hours, with occasional shaking. Identical results were obtained without pressure by the use of a freshly prepared solution of sodium ethylate. Herbig's experiments (*Ding. Poly. J.*, 1894, **292**, 42, 66) confirm these results so far as regards the saponification under pressure, but equally satisfactory results were not always secured by the use of sodium ethylate. Herbig found, further, that wool-fat contains esters that are easily saponified by alcoholic potassium hydroxide, and that, working under definite conditions, constant numbers for these are obtained. Heating over the naked flame was found to effect the result much more rapidly than by means of the water-bath, and the action is complete at the end of one hour's heating in a flask provided with a vertical condenser. By reason of its convenience, this method is often employed in the commercial valuation of wool-fats. The table on page 497 shows some results obtained in this way compared with those obtained by saponification under pressure. In the latter estimation, 2N alkali was used and the materials maintained at a temperature of 105 to 106°.

Estimation of Unsaponifiable Matter.—The separation of the ethereal layer from the aqueous solution of saponified wool-fat and recovered grease is troublesome, an intermediate stratum of a very persistent nature being formed. C. Rawson has suggested the following plan:

The sample is saponified in the usual way, and the resultant solution is evaporated in a porcelain basin placed over a small flame. Toward the end of the operation some powdered sodium hydrogen carbonate is stirred in to neutralise the excess of alkali, and some sand also added. The residue is then dried at 100° and exhausted with ether in a Soxhlet tube. The ethereal solution is then evaporated to dryness, the residue boiled with water, and the solution agitated with ether; or the ethereal solution is at once agitated with water containing a little sodium hydroxide to dissolve any soap it may contain, and then evaporated to dryness and the residue weighed.

A more satisfactory method is that of Herbig. From 1 to 2.5 grm. of the fat are boiled with N/2 potassium hydroxide for an hour, the excess of alkali neutralised with standard acid, and the whole washed into a beaker with boiling alcohol. The alcohol is evaporated, the solution heated to 70 to 75°, and the fatty acids precipitated with calcium chloride, the amount of which has been calculated from the saponification-equivalent. The precipitate is filtered off, well washed with dilute alcohol (1 to 20), and dried on the filter *in vacuo*. When dry, it is extracted in a Szombathy extractor with freshly distilled acetone for 6 hours, after which the acetone is evaporated, the extract washed with ether into a platinum basin, the ether evaporated, and the residue, which consists of the unsaponifiable matter and of the esters which cannot be saponified by the ordinary process of boiling with alcoholic potash, dried at 105° and weighed.

The chief points to be observed are the purity of the acetone—the fraction boiling between 55.5° and 56.5° being used—and the temperature at which the calcium salts are precipitated. If too hot they fuse, and if too cold they become slimy, subsequent filtration being almost impossible in either case.

It is advisable to extract the cork of the extraction apparatus with ether, alcohol, and acetone.

For the estimation of the alcohols, free and formed by the saponification, it is necessary to saponify under pressure, precipitate with calcium chloride, and extract with acetone as described.

F. Ulzer and H. Seidel propose to ascertain, instead of the saponification-equivalent, the total acidity number, as was recommended by Benedikt and Mangold in the case of wax. This number is the amount of potassium hydroxide (expressed as mg. per grm.) required to neutralise the mixture of fatty acids and fatty alcohols obtained by saponification and decomposition of the soap with acid. 20 grm. of potassium hydroxide are dissolved in 20 c.c. of water in a porcelain basin holding from 350 to 500 c.c., and the solution heated to boiling for about a minute, the heating continued on a water-bath until a thick, uniform soap is obtained, and the basin finally placed for 2 hours in the water-oven to complete the saponification. The soap is dissolved in about 250 c.c. of boiling water and decomposed with 40 c.c. of hydrochloric acid previously diluted with water. The clear fatty layer is repeatedly washed with boiling water until the washings are free from acid, and then dried in the water-oven. From 5 to 6 grm. of the dry mixture of fatty acids and alcohols are weighed accurately and titrated with *alcoholic* potassium hydroxide with the precautions noted above in the determination of the molecular weight. The authors conclude that for the technical examination of a wool-fat sufficient data are furnished by the estimation of the acid value (*i. e.*, the mg. of potassium hydroxide required to neutralise the free fatty acids of one gram), the total acidity number, the iodine number, and the Reichert-Meissl number, together with a gravimetric determination of the unsaponifiable matter.

Lewkowitsch (*J. Soc. Chem. Ind.*, 1892, **11**, 141, and *Chem. Anal. of Oils, Fats, and Waxes*) gives the following data from the analysis of a wool-fat: The volatile acids were estimated by the Reichert process and their mean molecular weight assumed to be 104 ($C_5H_{12}O_2$). The total free and combined fatty acids were well washed to free them from soluble fatty acids, and their molecular weight found to be 332.

Volatile acids from 1 grm. required,	0.124	c.c. normal KOH.
Free insol. acids from 1 grm. required	0.586	c.c. normal KOH.
Total insol. acids from 1 grm. required	2.19	c.c. normal KOH.
Combined insol. acids (by difference)	1.48	c.c. normal KOH.
Unsaponifiable matter	36.47	%.

And therefore.,

Volatile fatty acids = 0.124 × 10.2 =	1.26%
Insoluble free fatty acids = 0.586 × 33.2 =	19.45%
Combined insol. fatty acids (hydrated) = 1.48 × 33.2 =	49.13%
Total unsaponifiable matter	36.47%
	106.31%

The excess over 100% is of course due, in part at least, to hydration incident to the saponification.

Lanolin.—On account of its property of forming readily with water, an emulsion, wool-fat, purified by various patented processes, has come into extensive use as a basis for ointments and salves. Two preparations are recognized by the British and United States Pharmacopœias—*Adeps Lanæ* and *Adeps Lanæ Hydrosus*. It is commonly known as "lanolin," and consists of about 75 to 80% of wool-wax with 20 to 25 % of water. It is usually white or slightly yellow, and of salve-like consistence. It does not turn rancid. According to Liebrich, it should be free from all traces of chlorine, metals, glycerol or its esters, soaps, saline matters, and mechanically intermixed impurities or colouring matters, and it should not have any disagreeable odour. On rubbing on blue litmus-paper no reddening should occur.

Distilled wool-grease is a product obtained by distilling wool-fat with the aid of steam. The lighter portions, "olein," separated by cooling, are used for lubricating wool, and the more solid fractions "stearine," in the manufacture of soap and candles. It has also been used to adulterate tallow. According to Lewkowitsch (*J. Soc. Chem. Ind.*, 1892, **11**, 142), but a small proportion of the esters originally present in the wool-fat are found in the distilled product, the greater portion being decomposed into fatty acids and hydrocarbons.

$$\underset{\text{Cetyl palmitate.}}{C_{15}H_{31}COOC_{16}H_{33}} = \underset{\text{Palmitic acid.}}{C_{15}H_{31}COOH} + \underset{\text{Cetene.}}{C_{16}H_{32}},$$

Smith (*Ann. Chim. Phys.*, (3), 1842, **6**, 40). The fatty acids, especially the higher members of the series, are further dissociated into hydrocarbons and acids of lower molecular weight. Hydrocarbons are also formed by the decomposition of the free alcohols, a part of which, however, distil unchanged. The nature of these hydrocarbons is not well understood, it is, however, probable that they can be distinguished from hydrocarbons intentionally added by the estimation of the bromine addition and substitution numbers, the optical rotation and index of refraction. These constants, obtained on hydrocarbons separated from some distilled grease oleines by Gill and Mason (*J. Am. Chem. Soc.*, 1904, **26**, 665), are shown in the table below:

Oleine	Sp. gr.	Bromine		Optical rotation	Refractive index at 20°
		Addition	Substitution		
A	0.896	28.8	14.2	+17° 58′	1.4967
B pure	0.902	25.1	14.8	+17° 36′	1.4991
C	0.896	21.5	16.8	+15° 13′	1.4948
D (doubtful purity)	....	3.8	9.0	+2° 56′	1.4921
Mineral oils	0.848 to 0.863	4.4 to 5.9	5.6 to 8.4	+1° 25′	1.4662 to 1.4750

The extraction of these hydrocarbons is carried out as follows: 200 grm. of the oil are saponified by boiling on a water-bath 2 or 3 hours with an excess of alcoholic potassium hydroxide (120 grm. to the liter) in a 750 c.c. flask, provided with a return flow condenser. When the saponification is complete the solution is transferred to a liter separatory funnel and shaken several times with 300 to 400 c.c. of redistilled gasoline (86° B.) The soap solution is thrown away. The gasoline solution is concentrated to about 1/2 its volume and washed with warm water mixed with a little alcohol in the separatory funnel until all the soap is removed. The remainder of the gasoline is distilled off in the water-bath, and the residue heated to 130° in a porcelain dish to drive off the water and last traces of gasoline.

From the saponification numbers of the different oils, the requisite amount of alcoholic alkali is calculated, and 100% excess employed. After the saponification, when gasoline is first added and the mixture thoroughly shaken, no separation occurs, even after several hours' standing. Salt is without effect. Finally, water is added in small quantities until distinct layers formed. In washing the gasoline solution water alone was tried, but did not appreciably dissolve the soap. When warm water, mixed with a little alcohol, was used, the soap dissolved readily. In heating the oil to 130° to drive off water, a very small flame or, better, an electric stove should be used, and the oil constantly stirred to prevent bumping. A thermometer serves well as a stirring rod.

The unsaponifiable oil is freed from cholesterol and other higher alcohols by boiling for an hour with 100 c.c. of acetic anhydride in a flask provided with a return flow condenser, and heated over a sand-bath. Water is added, and the solution transferred to a separatory funnel where it is washed with water and alcohol until the upper layer is clear and no odor of acetic acid is perceptible. The cholesterol and higher alcohols are dissolved by the acetic anhydride, leaving the hydrocarbons.

After submitting the oils to this process, an estimation of their saponification number is made, and if more than 0.2 c.c. of alcoholic potash is used up, the treatment with alcoholic potash and acetic anhydride repeated.

The examination of distilled wool-grease is conducted upon the same general lines indicated in the case of wool-fat. Lewkowitsch obtained the following results from a sample obtained by the distillation of recovered grease, the analysis of which is stated on page 502.

Free fatty acids	54.91%
Combined fatty acids	7.02%
Unsaponifiable	38.80%

For other analyses of distilled wool-grease see page 409.

Alcoholic potassium hydroxide should be used in the determination of the molecular weight.

The fatty acids may also be determined with sufficient accuracy by the usual gravimetric method.

SOD OIL. DEGRAS. FRENCH DEGRAS (U. S.)

Dégras is the waste fat obtained in the chamoising process and largely used in dressing leather. The chamoising process consists essentially in oiling the suitably prepared skins with whale or cod oil (*i. e.*, the lower grades of codliver oil), stamping them in the stocks, and placing them in heaps, so that a fermentative change attended with development of heat is brought about. The process is complete when the skins have acquired the usual yellow colour of chamois leather. Under these conditions, oxidation of the oil takes place, and a portion of it combines with the skin, from which it cannot be removed by the usual solvents. About an equal quantity of uncombined oil is also mechanically enclosed in the skin. After being well scraped with a blunt knife, by which much of the excess of oil is removed, the skins are washed with lye and the emulsion treated with acid; the fatty matter which rises to the surface is added to the oil already obtained by scraping. The product so obtained constitutes the so-called "sod oil." This is the method largely used in Germany and England. The following process employed in France is also used in England to a considerable extent: The treatment by oiling, stocking, and fermenting is carried out for a shorter period, so that a larger proportion of uncombined oil remains in the skins. This is removed by wringing or hydraulic pressing, and constitutes the "moëllon" or "dégras" of commerce. The remaining uncombined oil is removed by washing with lye and treatment with acid, and is usually added to the product. The moëllon of commerce is said to be invariably mixed with untreated oils. Moëllon contains less fibre, mineral matter, and water than sod oil.

Jean found that dégras (moëllon) contains from 10 to 20% of water, and that the property of forming an emulsion with water depends upon the presence of an oxidation product of the oil formed during the chamoising process. He describes it as a "resinous substance," insoluble in petroleum spirit, but soluble in alcohol and ether. It is saponifiable, but, unlike ordinary fat, the soap formed is not precipitated from alkaline solution by the addition of salt. The m. p. was stated to be 65 to 67°. Simand has given it the name *dégras-former*. According to him it is insoluble in petroleum spirit, benzene, and almost insoluble in ether. It is soluble in alkaline solutions, from which it is precipitated by the addition of acid. It was also found in all animal and marine oils. Fahrion regards it as a mixture of hydroxy-fatty acids and anhydrides. It is an oxidation product, and experience has shown that those marine animal oils which absorb oxygen readily are the most suitable for the preparation of dégras. Fahrion found an iodine-absorption of 65.9% in dégras-former. Ruhsam found 98.8% in sample No. 1 on page 510. According to Fahrion, dégras-former contains no nitrogen, that found by Eitner being due to impurities.

Dégras-former is said not to exist in the free state in dégras, but forms a part of the saponifiable matter which is readily soluble in petroleum spirit, in which the dégras-former itself is insoluble.

Baron (*Rev. Chim. Ind.*, 1897, **8**, 225) prepares an artificial dégras as follows: 1000 kilos of neutral wool-fat (extracted by petroleum spirit) are placed in a tinned steel vessel with 5000 kilos of cod or whale oil. The liquid is heated by a steam coil, agitated for 3 hours, then allowed to rest and cool for the same period, and the water withdrawn. The water is again heated to 40°, 150 kilos of hydrogen peroxide and 450 kilos of water added, and the whole agitated for 5 hours at a pressure of 2 atmospheres. The resulting product is said to form an excellent moëllon, having a yellow colour and being easily emulsified and absorbed by the skins. It is important that the wool-grease be free from sulphuric acid, lest this should dissolve traces of iron, and so cause darkening of the leather.

Examination of Degras.—*Water* is ascertained, according to Simand, by weighing 25 grm. of the sample in a tared porcelain basin provided with a short thermometer as stirrer, adding 50 to 100 grm. of blubber or other oil previously dried by heating to 105°, heating the mixture to the same temperature, and determining the loss in weight. Ruhsam makes the estimation by heating 2 to 3 grm. of the sample in a weighed platinum crucible until an empyreumatic odor indicates the complete dehydration of the fat.

French dégras usually contains from 10 to 20% of water; sod oil may contain as much as 40%.

Free Acid.—*Mineral acids* may be detected as described on page 9. The amount is estimated by boiling a weighed quantity of the sample with water and separating the watery solution, which will contain the mineral acids as well as any soluble fatty acids; the determination of the former is made by adding methyl-orange and titrating with standard alkali until the point of neutrality is reached. The *soluble fatty acids* are then determined by adding phenolphthaleïn and titrating a second time.

Free fatty acids may be estimated in the residue insoluble in water by dissolving in alcohol and titrating as usual. They are usually calculated to oleic acid.

Ash.—This is estimated in the usual manner. It should be tested for iron. According to Simand, even as low a proportion as 0.05% of ferric oxide has a distinctly injurious effect.

The ash of moëllon is usually less than 0.1%; that of sod oil may amount to several %.

Fragments of hide may be estimated in the residue left from the solution in petroleum spirit, which is dried, weighed, and incinerated.

The loss on incineration may be taken to represent, roughly, the hide fragments.

Unsaponifiable matter may be estimated in the usual manner as described on page 79.

Degras-former.—Simand makes the estimation as follows: 20 to 25 grm. of the sample, according to the amount of water present, are saponified in an Erlenmeyer flask, with a funnel placed in the mouth, using a solution of about 5 to 6 grm. of solid sodium hydroxide in 10 c.c. of water and 50 to 60 c.c. of alcohol. The alcohol is evaporated, the soap dissolved in water, and the fatty acids liberated by hydrochloric acid. The liquid is then warmed until the fatty acids have formed a clear oily layer and the dégras-former has collected in lumps. It is then allowed to cool and the acid water separated from the undissolved portion This latter is washed several times with boiling water, the washings added to the acid liquid, and the mass remaining in the flask (consisting of the dégras-former, fatty acids, and unsaponifiable matter) is dried at 105°. The acid liquid and washings are neutralised with ammonium hydroxide, evaporated to dryness, redissolved in a small amount of water, the solution feebly acidified with hydrochloric acid and the small amount of dégras-former thus obtained (which had been dissolved in the aqueous liquid) separated by filtration, washed, dried, and added to the contents of the flask. It is then extracted with 100 to 120 c.c. of petroleum spirit, which dissolves the fatty acids and leaves the dégras-former and some albuminous materials. The residue is dissolved in alcohol by warming, the solution filtered, the filtrate evaporated to dryness, and the residue weighed as dégras-former. The process is said to be accurate within 0.5%. The petroleum spirit may be evaporated and the residual fatty acids weighed and examined.

Dégras, according to Simand, is pure and genuine only when it contains at least 12% of dégras-former. It may contain as much as 17%.

Jean ascertains the proportion of "resinous substance" as follows: A weighed quantity of dégras is saponified and the watery solution or the soap extracted with ether to remove the unsaponifiable matters. The soap solution is boiled to drive off the ether, and precipitated while hot with excess of pure sodium chloride. After cooling, the coloured liquid is filtered from the separated soap, the filtrate collected in a flask, and acidified with hydrochloric acid. The "resinous substance" separates in flocks, which on boiling unite and adhere to the side of the flask. The liquid is cooled, shaken out with ether, the ethereal solution evaporated, and the residue dried and weighed.

Jean considers that a sp. gr. of the oil extracted from dégras of less than 0.920 indicates the presence of foreign fats, *e. g.*, wool-fat, oleic acid, and tallow. The sp. gr. of the oil from dégras made from fish and whale oil is given as 0.949 to 0.955. The presence of tallow is also indicated by the higher m. p. of the fatty acids. In the examination of artificial dégras, Simand takes into consideration, in addition to the ash and water, the following points:

1. The dégras-former, which may be derived from a small quantity of admixed true dégras or from the oils.
2. The wool-fat.
3. Hydrocarbons (vaseline).
4. Colophony.

To determine the dégras-former, Simand proceeds as with genuine dégras, but substitutes ether for the petroleum spirit, since the wool-fat acids are dissolved by the former in the cold.

The estimation of the amount of wool-fat is as yet an unsolved problem. The detection of cholesterol would not, in itself, suffice, as it is a natural constituent of the fish oils used in the manufacture of dégras. Lewkowitsch points out that by the ordinary methods of saponification, a portion of the wool-fat would probably be found in the unsaponifiable portion, and that by again saponifying under pressure a definite saponification value would point to the presence of wool-wax.

Benedikt (*Anal. d. Fette u. Wachsarten*) states that by estimating the amount of cholesteryl acetate (see page 491) a very rough approximation of the amount of wool-fat may be obtained. Wool-fat furnishes percentages of cholesteryl acetate varying from 9.59 to 18.71%.

Resin may be estimated as on page 79, and hydrocarbons as on page 76.

Jean gives the following example of examinations of dégras:

	1	2	3	4	5	6	7
Water .... %	18.90	14.84	12.93	28.90	19.20	5.39	8.90
Ash .... %	0.25	0.13	0.55	0.70	0.07	0.25	1.21
Hide-fragments .... %	0.30	0.30	0.09	0.58	0.27	....	1.59
Oils .... %	69.71	74.65	80.00	66.93	75.66	84.87	72.15
Unsaponifiable matter..... %	6.84	6.05	....	....	....	....	....
"Resinous substance" .... %	4.00	4.05	5.81	3.52	4.80	9.46	16.15

Simand gives the following results:

		Dégras-former, %	M. p. of fatty acids, °	Soap, %	Original dégras	
					Hide fragments, %	Water, %
French dégras (anhydrous)	1	19.14	18.0–28.5	0.73	0.07	16.5
	2	18.43	28.5–29	0.49	0.12	20.5
	3	18.10	31.0–31.5	0.68	0.18	13.0
Sod oil (anhydrous)	1	20.57	33.5–34	3.95	5.7	35.0
	2	18.63	27.5–27	3.45	5.9	28.0
	3	17.84	28.0–28.5	3.00	4.5	30.5

The table on the following page give the results of an extended series of examinations of dégras by R. Ruhsam. Samples 1 to 9 are French artificial dégras; No. 10 is a so-called "emulsion fat"; No. 1 is a genuine dégras from the cod oil No. 12.

The iodine-absorptions were estimated as usual, the insoluble fatty acids being first freed from dégras-former by solution in petroleum spirit. It will be noted that the figure for genuine dégras is much higher than that of the artificial samples. The acetyl values were estimated by the method of Benedikt and Ulzer, and are of value only for comparison with each other.

The following shows the results of the examination of 12 sod oils found on the American market by Hopkins, Coburn, and Spiller (*J. Am. Chem. Soc.* 1899, **21**, 291.) The results are calculated on the water-free oil and the acids in mg. potassium hydroxide per grm. of oil.

	Water	Ash	Mineral acid	Oil, etc., sol. in petroleum ether	Soap, etc., sol. in alcohol	Hide fragments	Unsaponifiable matter	Oxidized acids	Free fatty acids
Minimum......	1.0	0.05	1.1	56.6	0.7	0.15	0.4	1.1	32.6
Maximum.....	40.6	1.0	91.5	96.6	8.8	3.0	42.6	26.4	34.3

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
No. of sample	Water, %	Iodine absorption, %			Acid No.	Saponification No.	Ether No. (difference between 6 and 7)	Constant acid No.	Constant saponification No.	Constant ether No. (difference between 9 and 10)	Acetyl acid No.	Acetyl saponification No.	Acetyl No. (difference between 12 and 13)	True acetyl No. (difference between 14 and 11)
		Dégras (anhydrous)	Insoluble fatty acids	Acetyllised fatty acids	Mg. of potassium hydroxide per grm. of anhydrous dégras			Mg. of potassium hydroxide per grm. of fatty acids			Mg. of potassium hydroxide per grm. of acetylised fatty acids			
1	19.1	74.7	70.5	73.1	37.7	....	....	185.5	224.3	38.8	181.0	280.0	99.0	60.2
2	12.9	64.2	58.6	52.7	72.7	110.4	37.7	102.8	131.5	28.7	92.6	164.7	72.1	43.4
3	12.4	77.4	75.4	90.4	40.2	110.7	70.5	129.6	172.9	43.4	128.9	196.1	67.2	23.8
4	15.9	78.4	70.2	66.6	50.1	134.8	84.7	162.9	193.7	30.8	157.0	237.0	80.0	49.2
5	16.4	77.8	78.5	76.2	52.7	137.4	84.7	163.5	185.9	22.4	160.9	227.0	66.1	43.7
6	11.5	76.6	76.5	75.7	64.9	108.8	43.9	175.8	229.6	53.8	171.0	282.5	111.5	57.7
7	13.9	96.7	95.9	88.9	......	....	....	182.5	215.6	33.1	178.7	212.4	33.7	0.6
8	17.3	83.7	93.4	102.7	28.9	100.8	71.9	96.7	197.1	100.4	92.8	175.4	82.6	....
9	16.6	80.9	....	....	52.0	141.2	89.2	....	....	....	....	....	....	....
10	5.3	74.4	79.3	73.0	54.1	125.2	71.1	179.5	210.2	30.7	180.1	217.0	36.9	6.2
11	......	127.7	142.3	127.4	......	163.8	....	180.8	212.2	31.4	176.8	228.3	51.5	20.1
12	......	126.7	106.0	101.9	......	186.0	....	159.3	213.2	53.9	158.2	215.7	57.5	3.7
Mean of 1–10	......	78.5	77.6	77.7	50.4	121.2	70.8	160.3 (except No. 8)	195.5 (except No. 8)	35.2 (except No. 8)	149.2	221.3	72.1	....

CLOTH OILS.

Cloth oil or wool oil is a trade term for all materials used in lubricating wool before spinning or rags before grinding and pulling. Since the success of the subsequent dyeing operations is in a great measure dependent upon the thoroughness with which these oils are removed by scouring, mineral oil, or, in general, any unsaponifiable matter is objectionable.

Mineral oils are emulsified by soap solutions and removed in great part, but not completely, by ordinary scouring (Matthews, *J. Soc. Chem. Ind.*, 1905, **24**, 659). With the better grades of goods even a small proportion of these oils is harmful, but with low grades it is permissible to use a strongly alkaline soap by which the mineral oil is to a great extent removed.

According to Horwitz (*Färb. Zeit.*, 1890, No. 11), cholesterol[1] may be present in the cheapest grades of olive oil in sufficient quantity to cause spotting of the dyed fabric. A sample of oil used to lubricate a wool which exhibited this condition was found to contain 3% of cholesterol,[1] and other samples were found to contain as high as 4%.

Olive, lard, and neatsfoot oils and commercial oleic acid ("red oil," "elaine," "oleine") are largely employed, and when of good quality are the most suitable. Besides these, however, wool-grease, distilled grease, and seek oil (the recovered grease from the scouring of various silk, woollen, and cotton goods) are employed. The cheaper oils in the market consist of one or more of the above, mixed with more or less mineral oil. So-called "emulsion oils," consisting of oil or "olein," held in suspension in a solution of soap, or of borax and Irish moss, and also simple solutions of soap are employed. The latter are prepared from castor oil or ricinolsulphuric acid.

An important factor to be considered in judging of the suitability of an oil for this purpose is its liability to cause spontaneous combustion. All oils that absorb oxygen are dangerous in this respect. Mineral oils, while not open to this objection, are still considered dangerous by reason of the facility with which a fire, once started, will spread in their presence. An examination directed to these points is all the more important in view of the higher rate of insurance which may be charged in some countries when oils considered unsafe in this respect are employed. In Great Britain the rating is based upon the nature of the oil, the proportion of unsaponifiable matter, and the flash test. The lowest rate is charged when an olive oil, lard oil, or "oleine" is used containing not more than 10% of unsaponifiable matter, or a fish or manufactured oil containing not more than 30% of unsaponifiable matter and having a flash-point not under 167°. The highest rate is charged in the presence of drying oils or of more than 50% of unsaponifiable matter.

---

[1] This unsaponifiable matter is probably phytosterol, as the researches of Lewkowitsch and Gill and Tufts (*J. Am. Chem. Soc.*, 1903, **25**, 498) have shown that cholesterol does not occur in olive and corn oils.

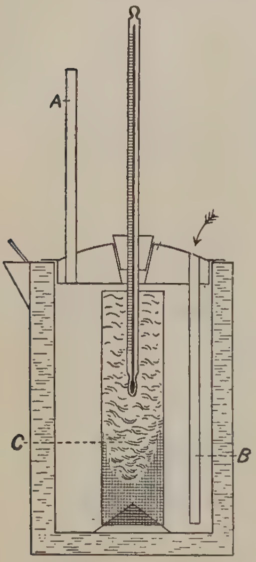

FIG. 14.

The "flash-point" of an oil intended for this purpose may be ascertianed easily by placing 50 c.c. in a porcelain dish or crucible, in a sand-bath, heating with constant churning, and noting the temperature at which a flash across the surface is produced when a small flame is brought near.

A satisfactory test of the liability of an oil to inflame spontaneously may be made by Mackey's "Cloth-oil Tester" (*J. Soc. Chem. Ind.*, 1896, **15**, 90; also Gill, *ibid.*, 1907, **26**, 185). This consists of a water-jacketed metal oven of the following dimensions: Outside, 8 in. high and 6 in. diam.; inside, 7 in. high and 4 in. diam. The tubes A and B are 1/2 in. internal diam. and 6 in. long measured from the lid. The depth inside with the lid on is 6 1/4 in. The lid is packed with asbestos wool, and the tubes serve to maintain a current of air. Care should be taken that the steam from the water jacket is neither drawn down B nor warms A. C is a cylinder of wire gauze (24 meshes to the in.) 5 by 6 in. forming a roll 6 in. long and 1 1/2 in. diameter. In it is placed 7 grm. of ordinary bleached cotton-wadding, previously impregnated with 14 grm. of the sample occupying the upper 4 1/2 in. of the cylinder.

The water being brought to the b. p., a thermometer is inserted in the oiled cotton contained in the gauze cylinder, which is then placed in the bath, the thermometer being allowed to protrude through a cork in the opening shown in the lid. The water is kept boiling and the temperature read at the end of an hour. An oil attaining a temperature of 100° or over at the end of this time is to be regarded as dangerous. The following are the results of experiments:

Oil used	Temperature at the end of			Maximum
	One hour	One hour fifteen minutes	One hour thirty minutes	H. M.
Cottonseed	125	242	....	242 in 1 15
Cottonseed	121	242	282	284 in 1 35
Cottonseed	128	212	225	225 in 1 30
Cottonseed	124	210	....	248 in 1 35
Cottonseed	116	192	200	200 in 1 30
Cottonseed	118	191	202	202 in 1 30
Cottonseed	117	190	194	194 in 1 30
Cottonseed	112	177	204	211 in 1 45
Olive, fatty acids	114	177	....	196 in 1 25
Olive, fatty acids	105	165	....	293 in 1 55
Olive, fatty acids	102	135	208	226 in 1 45
White Australian olive	103	115	191	230 in 1 45
Olive, with 1% free fatty acid	98	102	104	241 in 3 25
"Oleine"	98	101	102	110 in 2 8
"97% oleine"	98	100	102	172 in 3 15
Belgian "oleine"	98	99	100	173 in 3 16
Olive, neutral	98	100	101	235 in 5 15
Olive, neutral	97	100	101	228 in 4 30
Olive, neutral	97	....	101	235 in 4 55

Chemical examination of cloth oils is by application of principles and methods already given. An estimation of unsaponifiable matter is important, and if *hydrocarbons* are present the flash-point should be ascertained. The iodine number will aid in the detection of *drying oils*. The examination of commercial oleic acid is given in detail on page 406; it is to be especially tested for unsaponifiable matter and for linseed-oil acids. *Resin* should be looked for in the fatty acids separated from the saponifiable portion as described on page 77. See also under "Wool-fat" and "Distilled Wool-grease." Free mineral acid, which is especially apt to be present in commercial oleic acid, is objectionable on account of its corrosive action on card-teeth.

In the case of "emulsion oils" the fatty matter may be separated by treatment with acid and examined as above. *Gelatin* or *gummy matters* used in preparing the emulsion may be separated by addition of alcohol.

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